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Analysis, Testing and Development of Safe Cleaning Methods of Rusted Stone Material

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Abstract

Three different treatments were applied on several specimens of dolomitic and calcitic marble, properly stained with rust to mimic real situations (the stone specimens were exposed to the natural environment for about six months in contact with rusted iron). Thirty six marble specimens, eighteen calcitic and eighteen dolomitic, were characterized before and after treatment and monitored throughout the cleaning tests. The specimens were characterized by SEM-EDS (Scanning Electron Microscopy coupled with Energy Dispersion System), XRD (X-Ray Diffraction), XRF (X-Ray Fluorescence), FTIR (Fourier Transform Infrared Spectroscopy) and color measurements. It was also made a microscopic and macroscopic analysis of the stone surface along with the tests of short and long term capillary absorption.

A series of test trials were conducted in order to understand which concentrations and contact times best suits to this purpose, to confirm what had been written to date in the literature. We sought to develop new methods of treatment application, skipping the usual methods of applying chemical treatments on stone substrates, with the use of cellulose poultice, resorting to the agar, a gel already used in many other areas, being something new in this area, which possesses great applicability in the field of conservation of stone materials.

After the application of the best methodology for cleaning, specimens were characterized again in order to understand which treatment was more effective and less harmful, both for the operator and the stone material. Very briefly conclusions were that for a very intense and deep penetration into the stone, a solution of 3.5% of SDT buffered with ammonium carbonate to pH around 7 applied with agar support would be indicated. For rust stains in its initial state, the use of Ammonium citrate at a concentration of 5% buffered with ammonium to pH 7 could be applied more than once until satisfactory results appear.

Keywords: rust removal, sodium dithionite, ammonium citrate, sodium hexametaphosphate, calcite, dolomite

Resumo

Três tratamentos diferentes foram aplicados em vários provetes de mármore dolomítico e calcítico, com manchas de ferrugem tal como acontece em situações reais (os provetes foram expostos à intempérie durante cerca de seis meses em contacto com ferro enferrujado). Trinta e seis provetes, dezoito de calcite e dezoito de dolomite foram caracterizados antes e após os tratamentos e monitorizados durante os testes de limpeza. As amostras foram caracterizadas por SEM-EDS, XRD, FTIR, e medições de cor. Além disto, foi também realizada uma análise microscópica e macroscópica da superfície do material pétreo. Por fim realizou-se ainda um teste de absorção por capilaridade de curta e longa duração.

Realizou-se vários ensaios com o objetivo de compreender que concentrações e tempos de contacto seriam as mais indicadas para este fim, confirmando igualmente com o que existia escrito até ao momento sobre esta temática.

Procurou-se desenvolver novos métodos de aplicação dos tratamentos, ignorando os métodos usuais de aplicação de tratamentos químicos sobre substratos de pedra, que normalmente recorrem à pasta de celulose. O agar surgiu como uma alternativa, sendo um gel já utilizado em muitas outras áreas, contudo, é algo novo neste campo, mas que possuí grande aplicabilidade na área de conservação e restauro de materiais pétreos.

Após a realização dos tratamentos de limpeza verificou-se novamente as análises de caracterização de modo a perceber qual o tratamento que era mais vantajoso para o operador e para o material pétreo. Chegou-se à conclusão que o tratamento ideal para manchas muito intensas e com grande penetração na pedra será usar uma solução de 3.5% de SDT ajustando a um pH 7 com carbonato de amónia, com aplicação através de gel de agar. Para manchas de ferrugem no seu estado inicial, é indicada a utilização de citrato de amónia a uma concentração de 5% ajustando a um pH 7 com uma solução de amónia, sendo aplicado com um gel de agar.

Palavras-chave: remoção de ferrugem, ditionito de sódio, citrato de amónia, hexametafosfato de sódio, calcite, dolomite

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Symbols and Abbreviations

SDT	Sodium dithionite = Sodium hydrosulfite – $Na_2S_2O_4$
AC	Ammonium Citrate – $C_6H_{17}N_3O_7$
D	Dolomitic Specimen
C	Calcitic Specimen
XRD	X-Ray Diffraction
SEM-EDS	Scanning Electron Microscopy coupled with Energy Dispersive microscope
XRF	X-Ray Fluorescence
FTIR	Fourier Transform Infrared Spectroscopy
ATR	Attenuated Total reflectance

1. Introduction

1.1 Preamble

Ever since the Greek – Roman period, to the modern and actual period, white marbles, calcitic and dolomitic ones, have been widely used nearly in every major city in the world to construct monumental buildings, architectural facades, fountains, bridges, aqueducts and sculptures [1, 2, 3].

Despite the stone material resistance, the alteration of these materials is inevitable over time. The stone condition depends not only of its properties but mainly from external agents that can cause alteration, damage, decay, deterioration and weathering. This agents can be chemicals (such as, acid rains, pollution), environmental (such as, humidity, rain), biological (biological colonization) or due to external interventions (such as, products applied on stone in past restorations processes) [3, 4].

Amongst the huge set of mechanisms and agents of decay of the stone material in monuments, one can identify staining due to the contact with metals. These stains are one of the most challenging problems for cleaning since the products causing staining are not soluble in water [5, 6, 7]. Two of the most common stains are caused by contact with both copper and iron materials. The origin of copper-based staining is commonly linked to the corrosion of the bronze materials that are in contact with the stone, such as sculptures [8]. The second one is normally linked to the rusting of the architectonic elements such as grades, nails and supports [5]. The resolution of this last pathology represents the main issue of this dissertation.

The solution for this pathology should foresee a methodology, which can be controlled throughout the whole process of treatment. This procedure should be respected carefully in order to prevent physical and / or chemical changes in the stone material, such as abrasion of the surface and introduction of soluble salts [8, 9].

The main reason for the cleaning of iron stains rely on aesthetical reasons, giving a better visual appearance to the material, but above all, an effective cleaning intend to promote the stability of the object [7].

The main purpose of this thesis is the setup of an efficient and safe removal of rust from stone materials, specifically both calcitic and dolomitic marbles, largely used in the construction of built heritage. While a number of researches tested different chemical compounds, there is no definitive comparative assessment identifying an efficient and safe method, were cleaning on marble was achieved. In order to obtain that, some promising chemical products reported in the literature were used, exploring different application procedures. Mineralogical analyses on the stone specimens and rust stains characterizations were first performed with X-Ray Diffractometry (XRD). The evaluation of the tested methods was carried out through Scanning

Electron Microscopy coupled with Energy Dispersive Microscopy (SEM-EDS), X-Ray Fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FT-IR) in both reflectance and transmission mode, microscopic and macroscopic documentation of the surface, color measurements, short- and long-term capillary absorption according to EN 15801 standard [33]. The characterization was carried out before and after treatments. Advantages and disadvantages of the cleaning products were thus highlighted, having always in mind that the treatment should meet certain requirements including safety, efficiency, non-harmfulness for the stone, absence of undesired by-products and applicability to real cases by restorers.

1.2. Calcitic: [$CaCO_3$] and Dolomitic: [$CaMg(CO_3)_2$] marbles

The calcitic mineral is presented as having a rhombohedral (or trigonal) crystalline system, whereas the dolomitic mineral has a orthorhombic crystalline system. [8, 10, 11].

The calcite presents a perfect cleavage, with a hardness of 3 in Mohs`s scale, being represented normally in white. One fundamental aspect of the calcite is that the calcium ions present in the calcite are easily dissolved with acid [8]. According to its purity, it can present other compounds, such as Magnesium (Mg). When the ratio between the Mg and the Ca is about 50%, it is known as dolomite and it is less sensitive to corrosion by action of acids [10, 11].

1.3 Rust formation

Rust is formed when there is a source of iron and humidity big enough, so that the process of corrosion begins [7]. In a stone material, the origin of the rust stains can have the most varied origin. For instance, they may originate from elements used in building itself, such as grades, nails, supports, or even iron minerals present in the matrix of the stone, due to the process of formation of the stone material. As time goes by, these iron minerals can oxidize, with the presence of water, creating iron stains [5, 11, 12].

The fact that both stone and iron materials are exposed to rains creates ideal conditions for rust formation. With relative humidity above 65% iron dissolution is promoted, thus forming Fe^{2+} (colorless) and two free electron as shown in reaction (eq. 1), which is white in color or colorless [13, 14]. The formed electron and proton (H^+) will react with FeOOH (formed with iron, water and oxygen) to form Fe_3O_4 rust via reaction (eq. 2). Also, the Fe_3O_4 rust is generated by the reaction of the dissolved Fe^{2+} with FeOOH rust (eq. 3). Totally, the formation of Fe_3O_4 can be represented as reaction (eq. 4), creating the red/brownish stains typical of this oxidation product [7, 12, 13].

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(eq. 1)}$$

$$3FeOOH + H^+ + e^- \rightarrow Fe_3O_4 + 2H_2O \quad \text{(eq. 2)}$$

$$2FeOOH + Fe^{2+} \rightarrow Fe_3O_4 + 2H^+ \quad \text{(eq. 3)}$$

$$Fe^{2+} + 8FeOOH + 2e^- \rightarrow 3Fe_3O_4 + 4H_2O \quad \text{(eq. 4)}$$

1.4 Proposed treatments

Studies about this argument are not recent and a clear definition of a good treatment is not still defined [3]. A list of the treatments previously studied is reported in Appendix 1. After a revision of these treatments, it was concluded that in the best treatments for marbles the pH has been adjusted to pH 7-8, being this the fundamental point to avoid the dissolution of the calcite [3]. Besides the pH, another factor to be controlled is the contact time between the sample and the poultice: it should not be too long, to allow the operator to observe the results of the treatment [9].

Because of the insolubility in water, iron stains could be difficult to remove [5, 15]. The removal of this kind of stains may be performed by dissolving them in acids, by complexation, and chemical reduction with or without complexing agents [16]. Chelating agents will complex the metal ion facilitating its removal [7, 16]. It is important to use the appropriate chelating agent to avoid the dissolution of the calcite. In order to achieve that, it is necessary to observe the constants of dissolution of the stone material [3]. On table 1, the constant of dissolution of the Ca^{2+} is reported, as well as the Fe^{2+} and Fe^{3+}. The Fe^{2+} and Fe^{3+} ions have higher constants than the Ca^{2+} ion, making possible to remove the iron oxides without damaging the marble. In this table, it is possible to observe the solubility constants of the more common chelating agents in conservation and restoration. It is also possible to see that the EDTA is a very strong agent and it will dissolve the stone substratum. At the same time, the citrate will not theoretically make any damage on the stone substrate, but it will also have less power of action on the iron stains [3].

Table 1. Constants of dissolution of Ca^{2+}, Fe^{2+} and Fe^{3+} [3].

	pKsp*	Kf, Citrate	Kf EDTA
Ca^{2+}	8.35	4.68	11.0
Fe^{2+}	14.43	3.08	14.33
Fe^{3+}	37.4	12.5	24.23

Reducing agents can be used, to convert Fe^{3+} to Fe^{2+}, removing thus the iron stain by washing it with water. When deciding to use a reducing agent, it is necessary to take into account the potential of reduction of Fe^{3+} (which is +0.77V), while the reducing agent should present a lower potential of reduction. Once the iron is reduced to Fe^{2+} it can be washed away. An

effective washing of the stone surface should be taken, in order to avoid residual iron (II) ions on the stone which, after re-oxidation to Fe^{3+}, may again create new staining [7, 15, 17].

1.4.1 Sodium Dithionite

One of the cleaning agents chosen was sodium dithionite, $Na_2S_2O_4$, widely used in the industry for its reductive properties, such as in the dying of indigo and in the stripping of dyed fabrics and fibers. It is also used in the clay industry as whitening agent and in the removal of metal impurities and in the making of paper, functioning as a bleaching of yellowed fibers of cellulose, basic component of paper [7, 15, 18].

This product, in the field of conservation and restoration, is used to reduce Fe^{3+} of iron stains from various materials to Fe^{2+}, this latter being more soluble in water that can be removed more easily. This product has been used in the removal of rust stains from a great variety of inorganic materials, including clay, stone and minerals [7]. The first person to note this fact and to recommend its use in the removal of iron stains in marble was Stambolov in 1968 [19].

Since goethite (one of the most common forms of rust) has lower solubility than $Fe(OH)_2$ (10^{-41} against 10^{-15}), it is necessary to use a reducing agent, in order to remove the iron oxide [7]. With the purpose of understanding how reduction works, from Fe^{3+} to Fe^{2+}, it is important to observe the reaction of the dithionite ion ($S_2O_4^{2-}$) with the Fe^{3+} at slightly acid pH [14]:

$$2FeOOH + S_2O_4^{2+} + 4H^+ \rightarrow 2Fe^{2+} + 2HSO_3^- + 2H_2O \qquad \text{(eq. 5)}$$

One of the facts to take into account is the decomposition of sodium dithionite in solution, causing the acidification of the pH, which can dissolve the stone substrate. In order to avoid this, a buffered solution should be used (i.e. sodium bicarbonate), to keep the pH of the solution between 6/7 during the longest period of time possible [20, 21].

1.4.2 Sodium Hexametaphosphate

The Sodium Hexametaphosphate has already been used in the field of conservation and restoration for the cleaning of stone materials. It is a deflocculant/chelating agent with a weak aggression to the marble and it has a pH almost neutral. It is weaker than EDTA and for this reason is indicated for stones that contains calcium in its matrix. Good results in rust removal after several applications have been reported [22]. It is used in ceramic industry as it is necessary in several stages of the ceramic wet processing to obtain a good dispersion of the solid phase together with viscosity drop [23].

1.4.3 Ammonium Citrate

Organic acids due to their non-toxicity have played an important role in the field of conservation and restoration. In this case, they were considered as being effective to remove rust stains almost forty years ago. Despite the popularity of the ammonium citrate, its use, in the cleaning of monuments/sculptures of stone is very recent [24].

Some publications report ammonium citrate as effective in removing two types of dirt: dirt on limestone of Egyptian statues, medallions of French stone from the XVIII century and removal of iron stains in the case of the Metropolitan Club building in New York, as well as in the Temple of Love on Long Island [5, 24].

The efficiency of the ammonium citrate as a cleaning agent is due to its chelating properties; indeed, the citrate is able to complex various metals [15]. This is evident when observing the constant of formation (K_f) of the metal-citrate: Cu(II) > Fe(III) > Al (III) > Pb (II) > Zn (II) > Ni(II) > Co(II) > Cd(II) > Mn(II) > Mg(II) > Ca(II) > Fe(II) > Sr(II) > Ba(II). The values of the citrate with Fe(III), Ca(II) and Fe(II) are 12.5, 4.7 and 3.1 respectively [3, 24].

As shown in Table 1, the pK_{sp} of Fe(III) is about 37.4, meaning that AC should have some difficulty in the complexation of Fe(III); the complexation of Fe(III), could be due to the counter-ion ammonia, which is known for being a good chelating as independent agent, for example, when used to complex copper [24].

Despite the fact that the formation constant of Ca(II) is higher than the calcium-citrate (8.35 and 4.68 respectively), the attack of citrate to the calcareous stone could occur, dissolving the calcium and bringing it into the solution, aspect already outlined in literature [24].

2. Experimental Design

The experimental design developed is divided essentially in three parts, as reported in the Figure 1. The description of all reagents, experimental methods and equipment used is reported in Appendix 2.

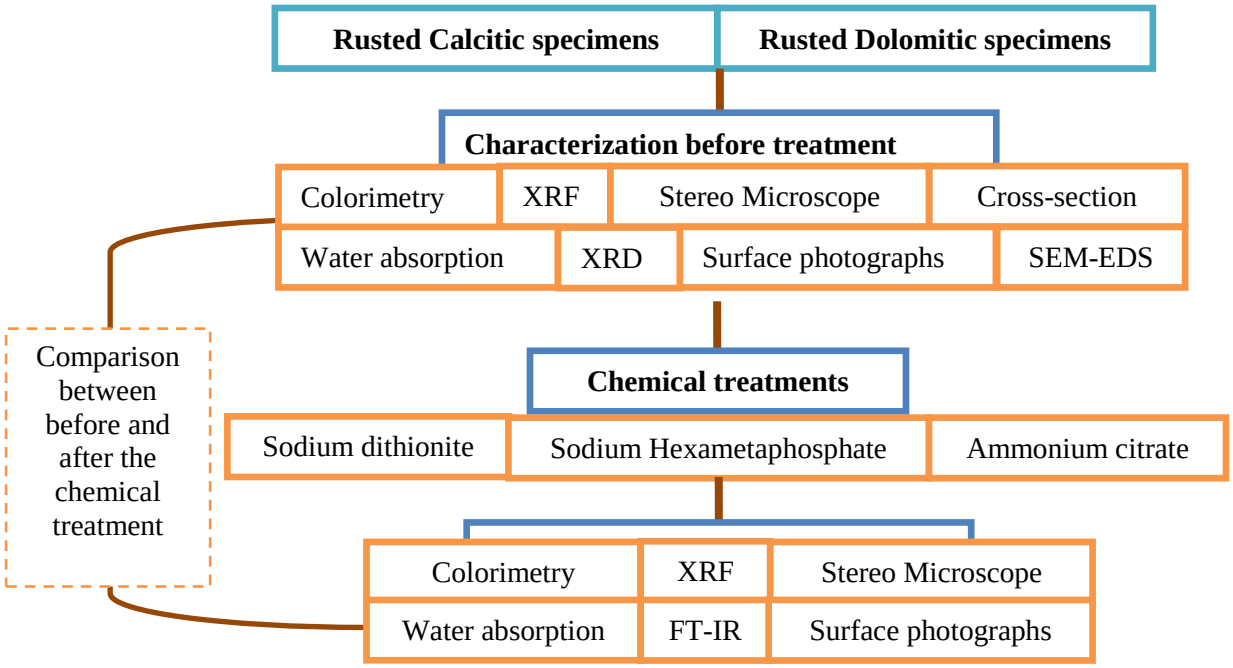

Figure 1. Experimental design.

2.1 Specimens

Two types of marble were used, one dolomitic and the other calcitic with the dimensions of 5x5x2cm as shown in Figure 2. These samples were left in the open air, exposed to the natural environment for about six months in contact with rusted iron. In these conditions they get rusty as natural as possible, exactly as if it happens in a building. Before analyzing them, specimens were washed in order to remove extraneous materials from the surface, leaving only the rust stains penetrated in the stone material.

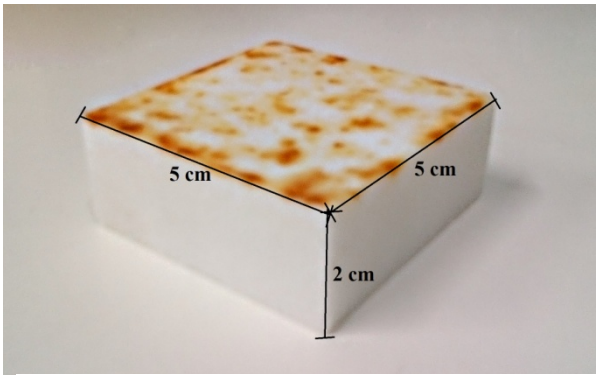

Figure 2. Specimen measurements.

The total number of specimens used in this experiment was 36 excluding those used in the trials for which the samples were only characterized through photography. For each type of marble a set of 18 specimens was selected. Each set was then divided among the treatments, but there was a leftover of three of each kind without rust so that they could serve as a reference. The distribution of these specimens according to the applied treatment is reported in Appendix 2.1.

2.2 Characterization of the specimens before treatment

In order to do this work there was a necessity of characterizing the specimens before the application of the cleaning treatment to gather a set of information for characterizing the state of the stone substrate and, at the same time allowing the analysis of the rusty spots. The process of characterization started with color measurements, so that a reference of the initial state of the surface of the specimens existed. This experimental essay process is described in Appendix 2.4. The preparation of the specimens for the stereo microscope was done afterwards, so that a comparison between the before and after treatment could be made. This experimental process is described in Appendix 2.4.

The characterization of the specimens involved SEM-EDS, XRF and XRD analysis, both to characterize the stone substrate and the kind of iron compounds present in the specimens. This experimental process and equipments used is described in Appendix 2.4.

2.3 Application of treatments

The treatments were applied according to the general guidelines reported in the literature. However, before applying the treatments in the characterized specimens, some preliminary tests were conducted in order to verify if the described conditions, such as, contact time and concentrations, could in fact, give the results presented in the bibliography. The obtained results by these trials are reported in the Appendix 3.

In order to identify the best concentrations and contact times, each cleaning agent was used with two different concentrations and two different contact times selected from the preliminary tests. Therefore it was possible to observe if a longer period with a lower concentration was better or worse than a lower period with a higher concentration. The experimental method can be found in the Appendix 2.2. In the table 2 the chosen treatments are reported.

Table 2. Treatments applied.

Cleaning agent	Concentration	Contact	pH	Buffer agent	Poultice

		time			
Sodium dithionite	3.5% 7%	3 hours 6 hours	6/7	Sodium bicarbonate	Cellulose
Hexametaphosphate	10%	2 hours	7	Ammonium 30%	Cellulose
Ammonium Citrate	2% 5%	24 hours	8	Ammonium 30%	Cellulose

After carrying out the first set of treatment using cellulose as support, the use of agar as poultice was tested in order to improve the efficiency of treatments. Agar is a non-toxic material from organic raw materials, extracted from several types of red seaweeds. The product is made of two polysaccharides, agaropectin and agarose [25]. Due to its gelling properties, agar is applied in different fields of industry, such as, pharmacy, biology, food industry and chemistry. To exploit as much as possible of his gelling capabilities, the water should be heated up to 80ºC before adding agar. After this stage, it will progressively develop a random coil structure that will rearrange at the cooling stage forming a rigid gel [26].

For the field of conservation and restoration, the agar poultice can be prepared as a water-based poultice or with chemicals such as, chelating agents, to create gels characterized by a variable pH for the treatment of specific substrates. This gel will act like a sponge, draining all the material dissolved by the chemical used into the matrix of the agar [27].

The better thing about agar is that, depending on the situation, it could be applied on different ways, so, if the user wants to apply it by brush on a surface, just needs to apply it when the temperature is above 40ºC. If the user wants to use it as a thin film, just has to lay it down on a plastic film and let it rest until the temperature is under 40ºC. The removal at the end of the procedure is facilitated by the low adhesion to the substrate, and it leaves almost no residues on the surface [27].

The preparation of agar is not as easy as cellulose poultice, however if it is prepared in the proper way, better results can be obtained. This way of operation gives advantages to the operator; an example of the evolution of the treatment can be checked in the results part (Figure 19). The use of agar was tested with the Ammonium Citrate and with Sodium dithionite. In the case of Hexametaphosphate, the film of agar was not formed, since this cleaning agent acts as a deflocculant, not allowing the union of the agar fibers.

Besides the poultice improvement, another one was obtained using a different buffer for Sodium Dithionite treatment. Analyzing trough FTIR the cellulose poultice with Sodium dithionite and Sodium hydrogen carbonate after performing the FTIR analysis of cellulose poultice with

Sodium dithionite and Sodium hydrogen carbonate, the presence of sodium salts was observed. The alternative found to try to reduce the amount of salt was to use ammonium carbonate as a buffering agent.

2.4 Characterization of the specimens after the treatment

After the application of the treatments, the characterization of the specimens was repeated in order to understand how these treatments affected the specimens, in terms of color, iron and/or salt residues. Thus, it was possible to determine either the treatment was good, or it was good to clean but left some residues in the stone material. The procedure was identical to the one used for the characterization of samples before the treatment, adding only the FTIR analysis.

3. Results and Discussion

3.1 Specimens characterization

The color measurements revealed what was already possible to observe through a naked eye. The specimens present in general a high level of red and yellow. The Table 3 and 4 present the average value for L*, a* and b* related to stained (C1 and D2) and unstained (C17 and D17) specimens. Lightness L* values range from L*=0 (black) to L*=100 (white). The value a* covers the red-green range. Values of a*>0 represent the red component while values of a*<0 represent green. The yellow-blue range is covered by the value of b*, b*>0 represent yellow while b*<0 represent blue [28, 29, 30].

In this case, it is possible to denote a slight dimming when the color of specimen C1 is compared with that of C17. A positive increase in the values of a* and b* when compared with the non-stained one, means that the surface has acquired stronger tones of red and yellow. The two values of a* and b* is translated into a deep orange coloration.

In Figure 3, the values are presented in the Table 3, relating to the points analyzed in this specimen which corresponds to calcite stone material, comparing them with specimen that serves as reference (not stained), on the right.

Table 3: Color measurements of the stained and unstained calcitic specimens.

Stained calcitic specimens				**Unstained calcitic specimens**			
Specimen - Point	L*	a*	b*	Specimen – Point	L*	a*	b*
C1 - 1	79,34	0,51	12,99	**C17 – 1**	82,74	-0,70	-0,86
C1 - 2	74,48	4,69	29,27	**C17 – 2**	81,90	-0,78	-0,47
C1 - 3	75,02	3,96	24,49	**C17 – 3**	81,97	-0,61	-0,88
C1 - 4	75,66	2,95	26,26	**C17 – 4**	80,50	-0,72	-0,03

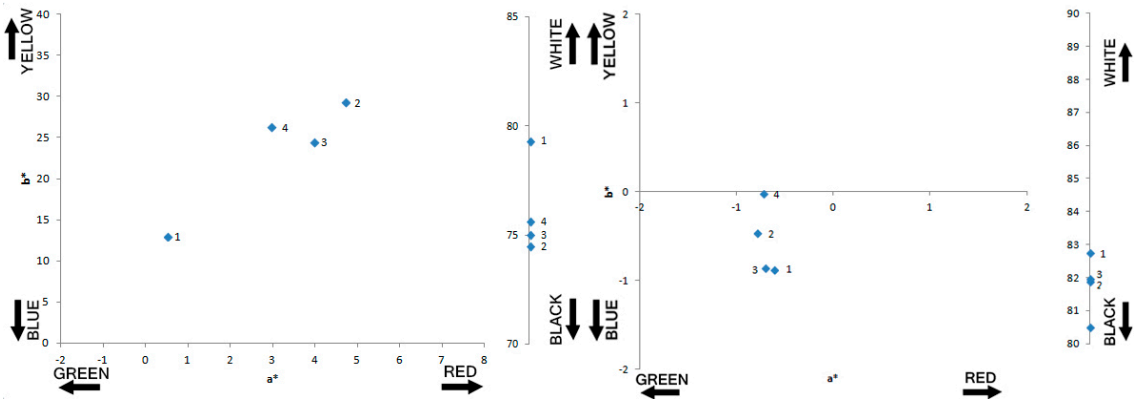

Figure 3. Values of the L*, a* and b* chromatic coordinates corresponding to the 2 different specimens (C1 and C17, respectively).

In the cases of the dolomitic specimens, rust coloration is stronger and deeper in respect to the previous one, the values are around in most cases to L* 50-70, a* 10-20 and b*20-40.

Table 4: Color measurements of the stained and unstained dolomitic specimens.

Stained dolomitic specimens				**Unstained dolomitic specimens**			
Specimen - Point	L*	a*	b*	Specimen – Point	L*	a*	b*
D2 - 1	85,11	0,60	7,04	**D17 – 1**	86,68	0,03	1,25
D2 - 2	68,86	14,63	40,79	**D17 – 2**	86,84	0,23	1,52
D2 - 3	79,75	3,60	18,56	**D17 – 3**	86,61	0,05	1,61
D2 - 4	52,32	26,38	42,11	**D17 – 4**	86,21	0,09	1,41

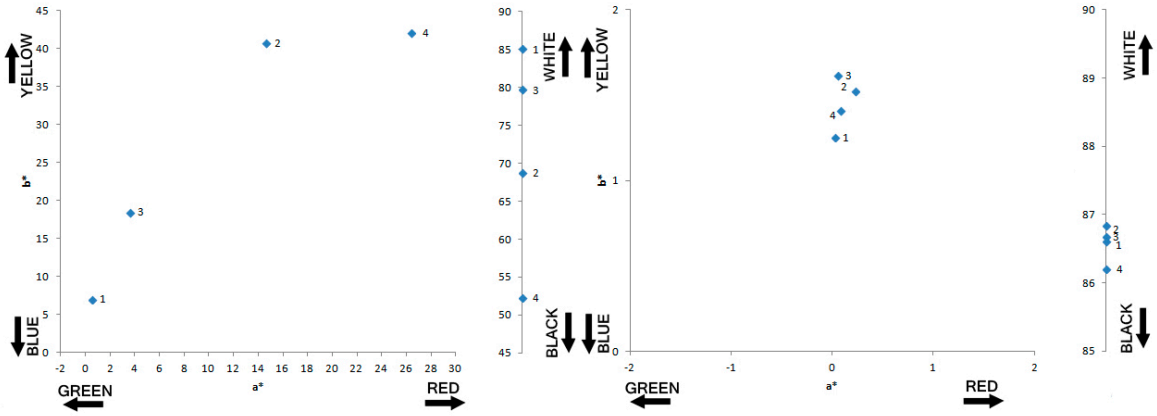

Figure 4. Values of the L*, a* and b* chromatic coordinates corresponding to the 2 different specimens (D2 and D17, respectively).

It is possible to verify in the two figures above that the one on the left side is darker than the one on the right side, with L* lower than 85, whereas in the reference specimen the L* values are above 86. In the case of green/red levels, it is visible that the values tend to the red color, while in the reference specimen, they are around 0. In the blue/yellow levels, in the rusted one, these tend to yellow, whereas in the reference specimen, the value is again around zero.

A water absorption test was made in order to understand the porous behavior of the stone material. This is a helpful tool to evaluate if the treatments applied changed the porosity of the stone material [31]. The test was conducted using two different methods: i) short period of contact time, 1 minute measurements; ii) the long contact time. Despite all the care taken, some of the values presented in the first absorption test present a slight difference between them; this could be due different porosity of the stones or some external defect on the measurements such as temperature or humidity. In the Figure 5 the values for calcitic and dolomitic stones respectively are presented.

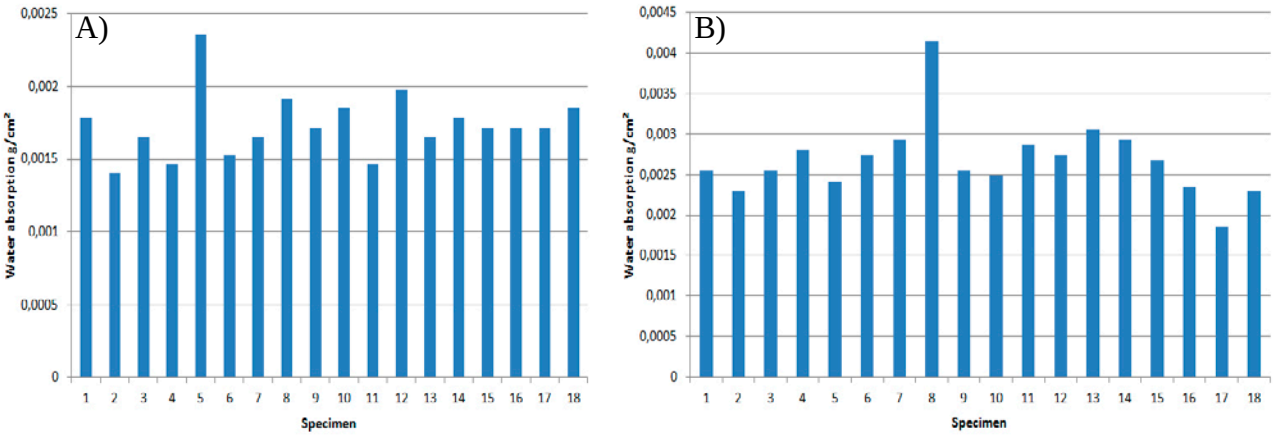

Figure 5. One minute water absorption g/cm^2 **A)** Calcite **B)** Dolomite.

The long term absorption revealed what was expected. The calcite specimens (Figure 6-A) absorbed a lightly lower amount of water respect the dolomitic stone (Figure 6-B).

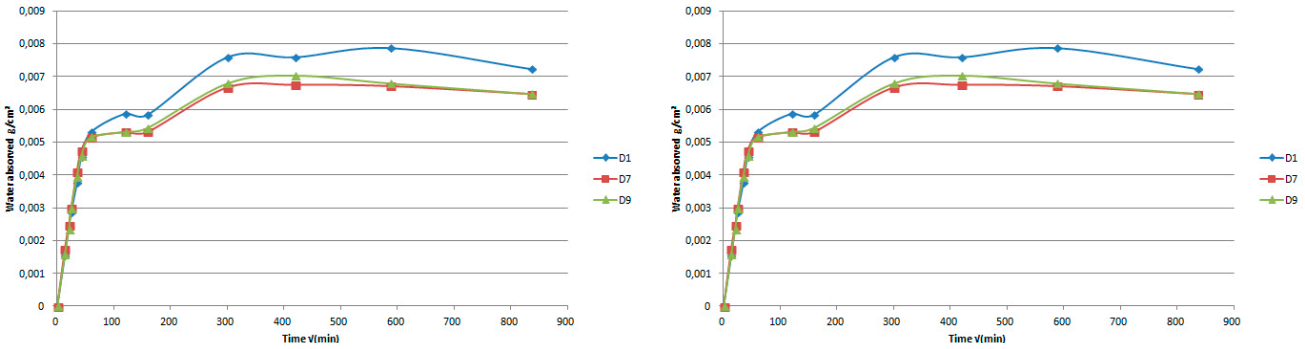

Figure 6. Long term water absorption g/cm$^{2.}$ **A)** Calcite **B)** Dolomite.

Xrf was conducted to evaluate the elements present in the stone substrate.

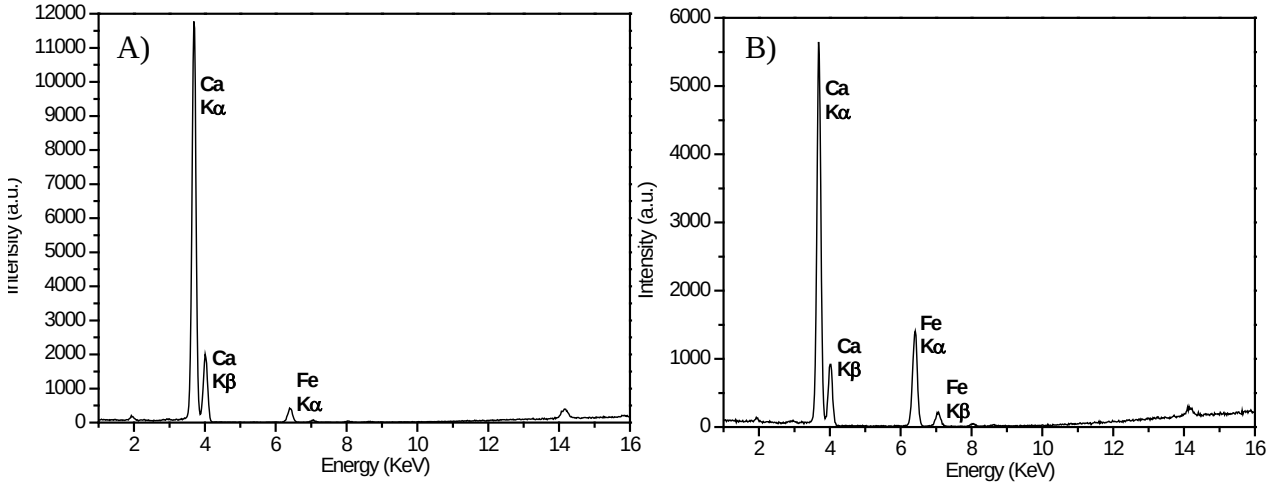

Figure 7. XRF spectra of **A)** specimen C1 point 1 and **B)** specimen D1 point 1.

In Figure 7 peaks are shown corresponding to Calcium (calcitic specimen) and Calcium and Magnesium (dolomitic specimens) respectively. Through the analysis of the specimens by XRF, the presence of iron was qualitatively assessed (peak at about 6.40 keV), as well as calcium (3.70 keV), with a more intense peak since this is the main constituent material of the stone substrate. The Magnesium (Mg) was not possible to detect due to the equipment sensitivity.

Through X-ray diffraction (XRD) it was possible to confirm that the constituent materials are calcite and dolomite ─ the XRD spectra are reported in Figures 8 and 9 respectively. The red line represents the specimens used in this work, while the blue line represents a pattern of calcitic material, used as reference in the database of the institution.

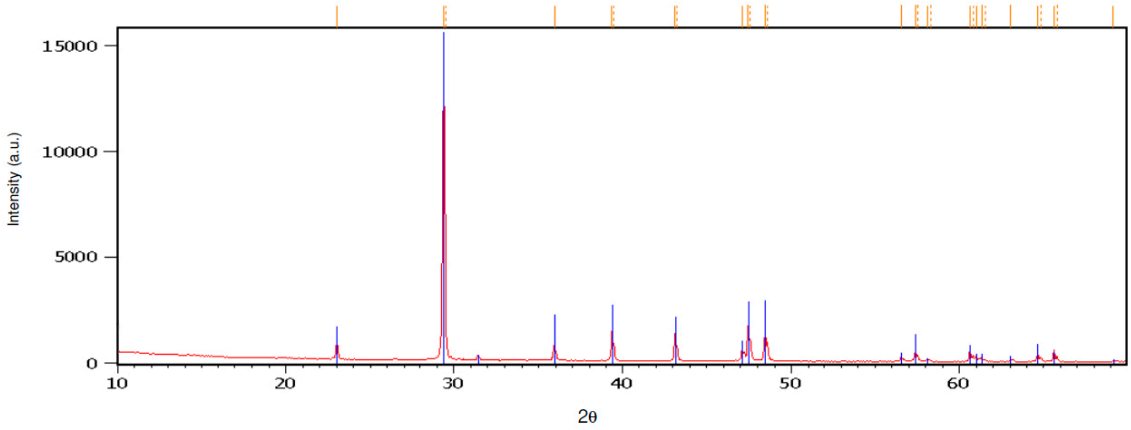

Figure 8. Diffractogram of $CaCO_3$ specimen (—) vs standard $CaCO_3$ diffractogram (—).

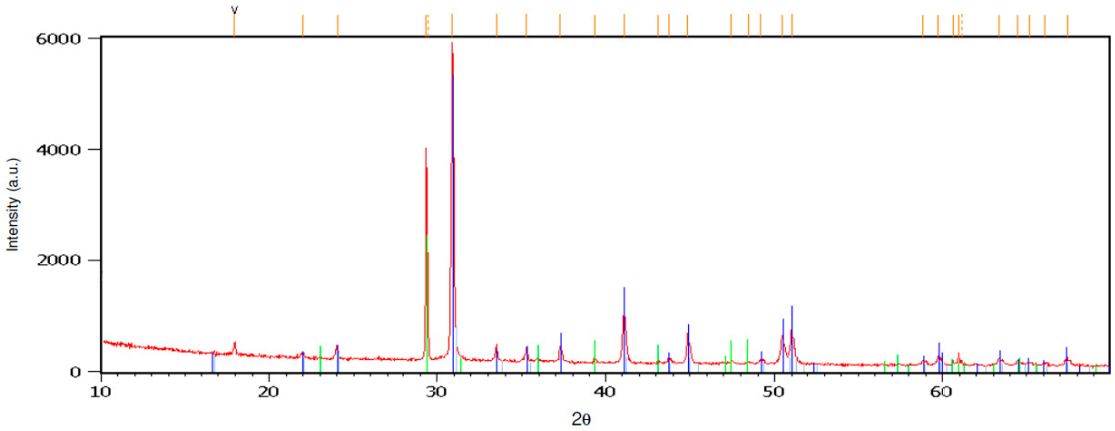

Figure 9. Diffractogram of $Mg(CaCO_3)$ specimen (—) vs standard $Mg(CaCO_3)$ diffractogram (—) vs standard $CaCO_3$ diffractogram (—).

The presence of dolomite (red line) was evident when compared with the dolomite diffraction pattern (blue line). Besides this, it is also displayed the reference diffractogram for calcite (in green). Moreover, the typical XRD pattern of calcite is also present, which has some peaks in common with the detected diffraction pattern of the mentioned sample of dolomite.

Despite the fact that the stone material analyzed contains rust, it has not been possible to detect the type of ferrous oxides present in the substrate. Even though, a small area of the specimen

surface, where the presence of rust was abundant, had been removed in order to be milled and subsequently analyzed, the result obtained was the same; it wasn't possible to detect any type of ferrous oxides.

3.2 Rust stain characterization

Through observation under the stereo microscope and through photographs of the surface it is evident that rust stains have different intensities and different forms, and essentially circular predominant form. In Figure 11 the surface of specimen C7 at different magnification is reported. All the others specimens are reported in appendix 4.

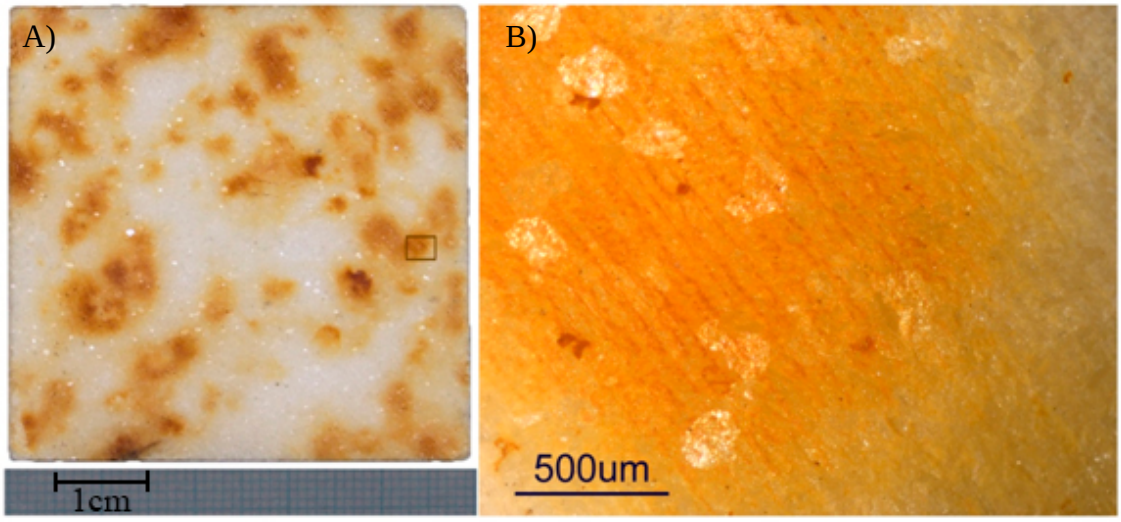

Figure 10. A) Surface photograph specimen D1 **B)** Optical microscope specimen D1.

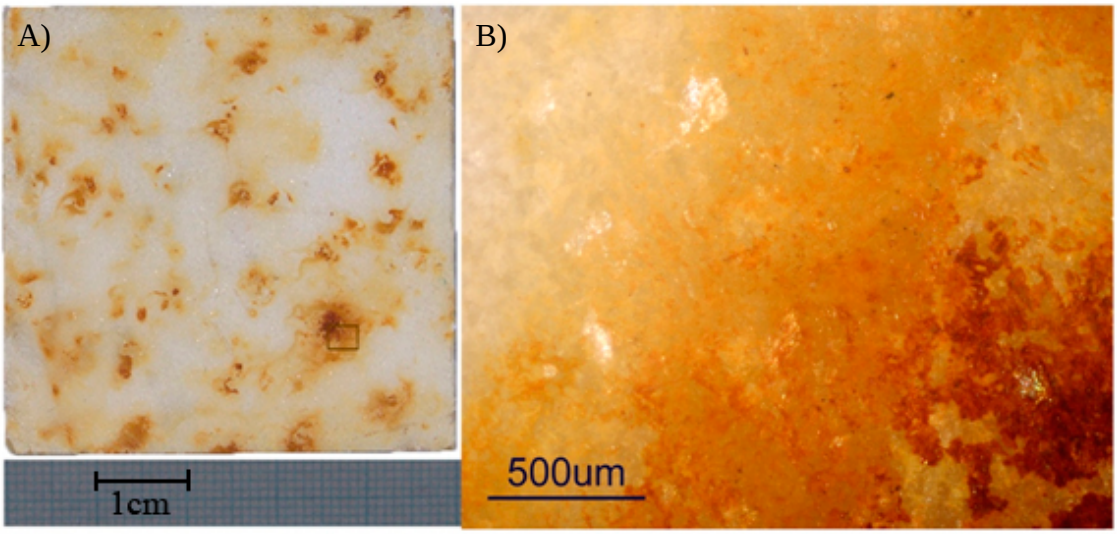

Figure 11. A) Surface photograph specimen C7 **B)** Optical microscope specimen C7.

The penetration depth of rust staining it is greater for dolomite respect to calcite as can be seen from the observation of cross sections in Figure 12. Probably this is due to the slightly different porosity of the two stones different crystals dimension (larger for dolomite respect to calcite).

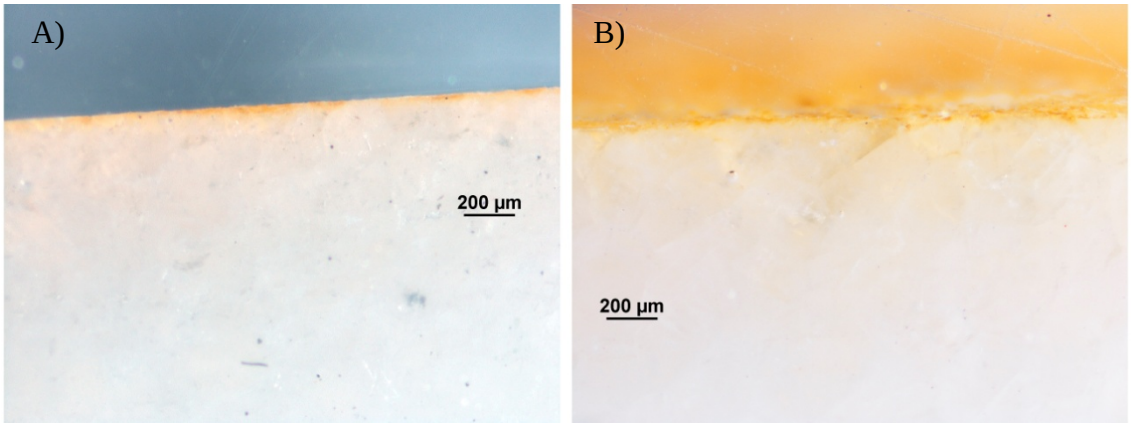

Figure 12. A) Cross-section specimen C15 **B)** Cross-section specimen D15.

SEM analyses were not conclusive. All the samples analyzed by this technique revealed what is possible just a little amount of iron, possible represented in the whitish color in the stone surface.

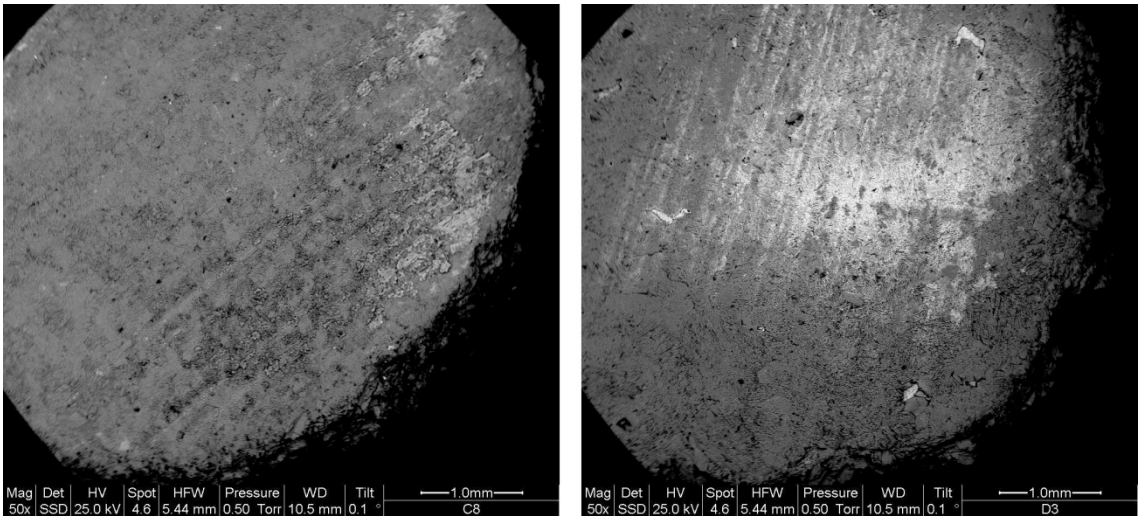

Figure 13. SEM-EDS **A)** specimen C8 **B)** specimen D3.

3.3 Chemical treatments

3.3.1 Sodium dithionite

In Figure 12 the results of the sodium dithionite cleaning intervention are present. The surface cleaning was more efficient using 3.5% solution respect to 7% solution. The contact time and solution concentration was the key factor in the removal process. It was proved that is better to have a longer time of contact with lower concentration (6 hours and 3.5%), instead a shorter

time using higher concentration (3 hours and 7%) in the case of deep rust. In the superficial rust, presented essentially in the calcite specimens, the 3 hour treatment was sufficient and the complete cleaning was achieved. In Figure 14 it is possible to compare the different results for the two treatments.

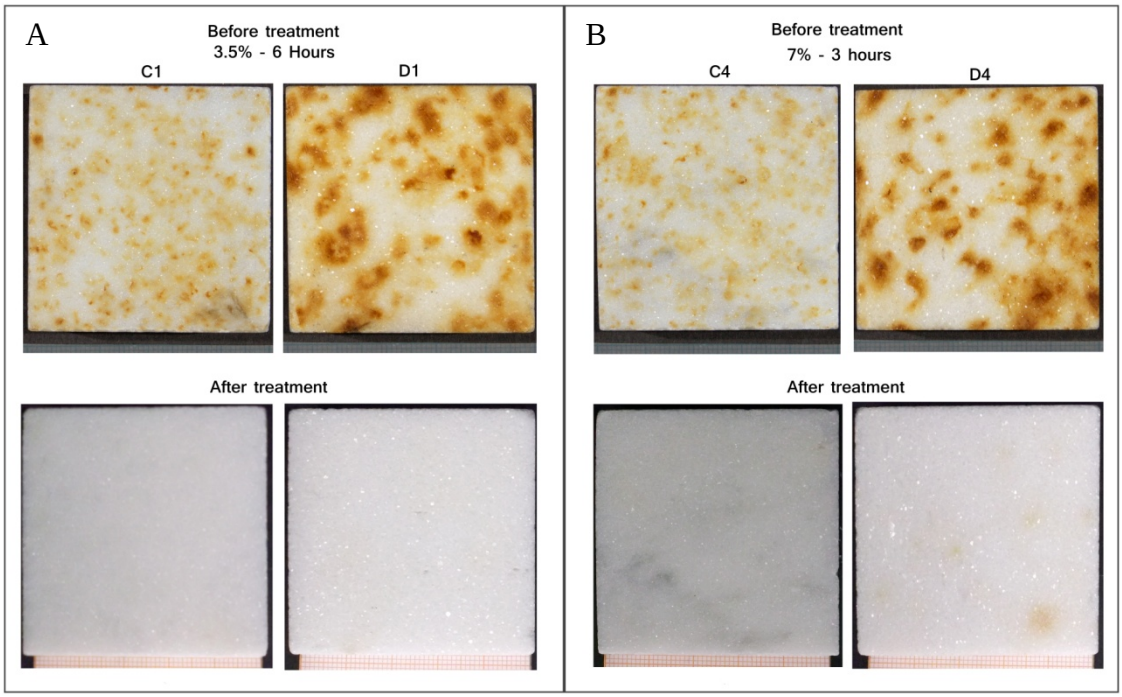

Figure 14. Comparison between treatments **A)** SDT 3.5% - 6 hours **B)** SDT 7% - 3 hours.

Another important factor was the buffer used. It is very important to use a buffer allowing stabilization of the pH for a long period of time, which is difficult in such solutions where the decomposition of the SDT is very fast. The pH was buffered for two reasons: i) pH ≈ 7 because the SDT is very reactive with oxygen if the pH is too low; ii) the dissolution of calcite is favored when the pH values is under 7.6 [3, 12]. It is advisable to achieve 7.6 pH value, seeking to maintain the pH of the solution without variation, which could lead to a greater dissolution of the stone material. Calcite is more sensitive to these variations in pH, while dolomite is less sensitive to pH changes. The buffer used was Sodium Carbonate and trough the stabilization of pH, it was possible to maintain stable the solution of SDT.

Although the treatments were effective, the evidence is that the most important factors are pH and the SDT, used product. The fact that the buffer used has sodium in its base, it is not very beneficial for the stone material due to its salts. The salt's crystals inside the pores can generate stresses that can turn stone into powder [32]. After the removal of the treatment, the material remaining on the Japanese paper was analyzed by means of FTIR in transmittance mode (Figure 15), being evident the large amount of sodium sulfate.

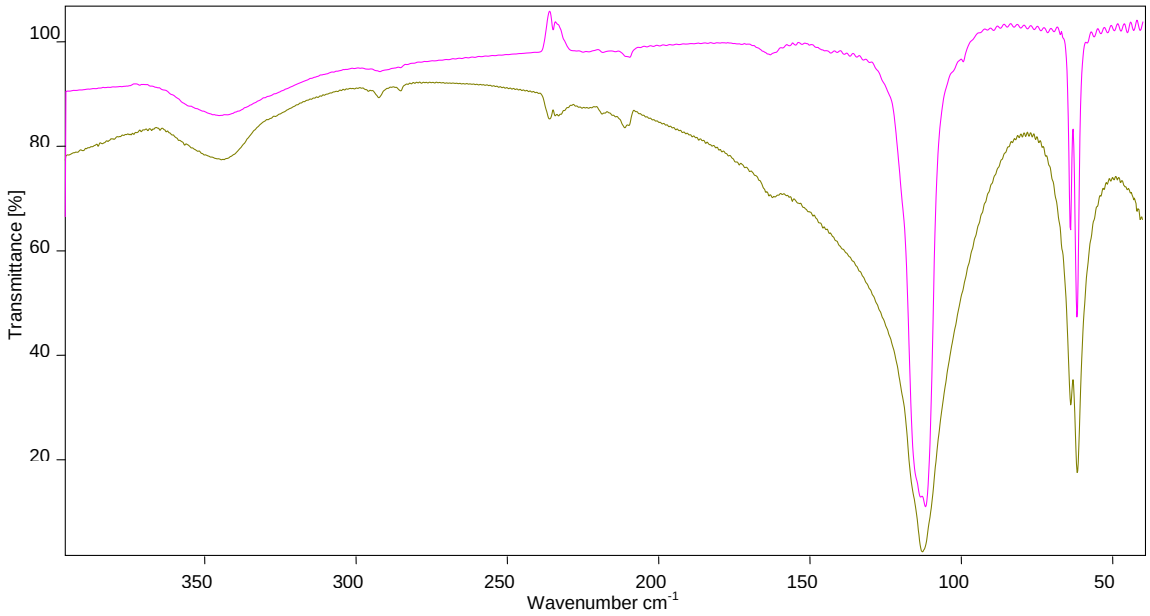

Figure 15. Infrared spectra (—) SDT 7% poultice powder buffered with sodium hydrogen carbonate (—**)** and sodium sulphate pattern.

Despite this, the analysis of the surface of the stone material by FTIR, did not revealed any sulfate. This confirms the importance of a good washing of the stone substrate after applying the treatment, not only because of possible total removal of cleaning agents still on the stony substrate, but also it allows the removal of the Fe^{2+} deposited on the sample surface.

Through repetition of colorimetric tests, it was possible to understand how the color of the specimens changed and how they were similar to standard specimens. In Table 5 and Table 6 the colorimetric data after cleaning compared with the standard specimens are reported. After the treatment, the recovery of the color was almost complete. The remaining results regarding color measurements performed in this treatment can be found in summary table in the appendix 4.

Table 5. Color measurements of the cleaned and unstained calcitic specimens.

Cleaned calcitic specimens				**Unstained calcitic specimens**			
Specimen - Point	L*	a*	b*	Specimen - Point	L*	a*	b*
C3 - 1	81,57	-1,40	4,57	**C18 - 1**	82,94	-0,68	-0,93
C3 - 2	80,32	-1,45	4,88	**C18 - 2**	81,36	-0,70	-0,84
C3 - 3	81,85	-1,53	4,24	**C18 - 3**	79,54	-0,662	-0,98
C3 - 4	82,24	-1,28	2,86	**C18 - 4**	82,04	-0,66	-0,86

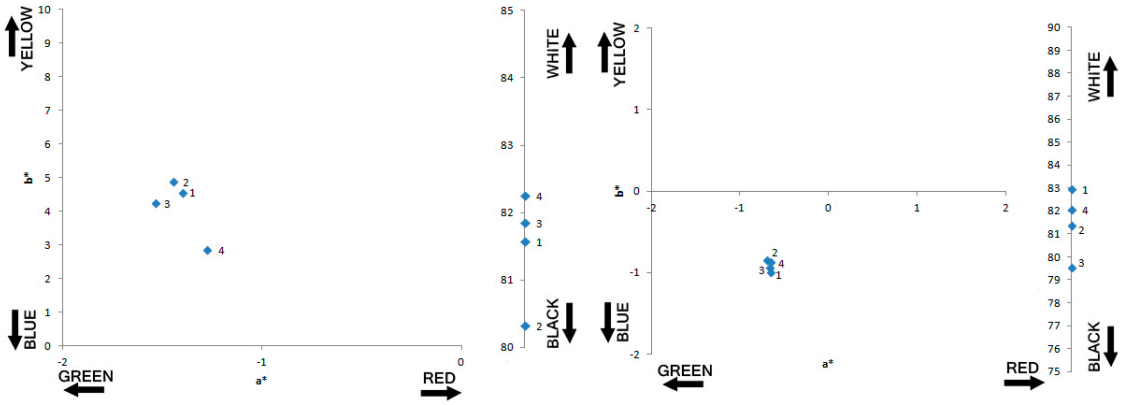

Figure 16. Values of the L*, a* and b* chromatic coordinates corresponding to the 2 different specimens (C3 and C18, respectively).

Table 6. Color measurements of the cleaned and unstained dolomitic specimens.

Cleaned dolomitic specimens				**Unstained dolomitic specimens**			
Specimen - Point	L*	a*	b*	Specimen - Point	L*	a*	b*
D1 - 1	87,04	-0,39	3,08	**D16 - 1**	87,61	0,13	1,46
D1 - 2	86,28	-0,43	7,71	**D16 - 2**	87,91	0,11	1,45
D1 - 3	85,95	-0,45	8,34	**D16 - 3**	87,55	0,15	1,59
D1 - 4	86,99	-0,55	6,38	**D16 - 4**	87,95	0,09	1,44

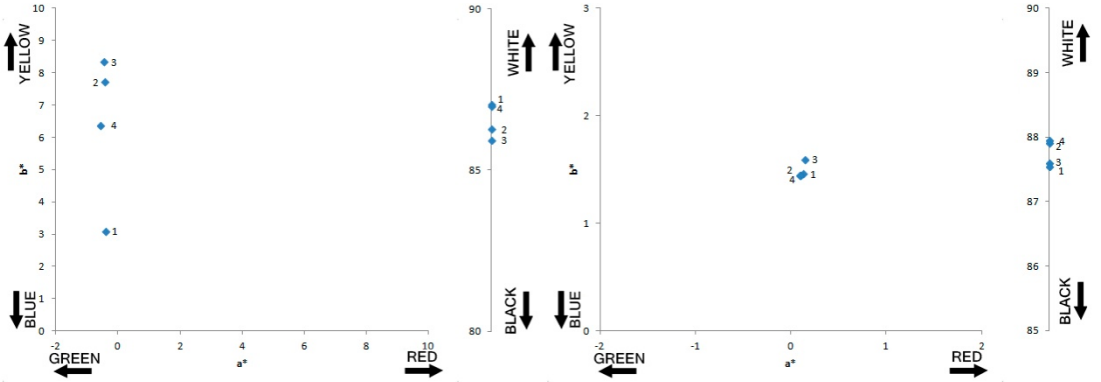

Figure 17. Values of the L*, a* and b* chromatic coordinates corresponding to the 2 different specimens (D1 and D16, respectively).

In the case of dolomitic samples for which the rust stains were more penetrated, it was more difficult to achieve the same results as that for calcitic marble. Despite this, to the naked eye, the result was very impressive.

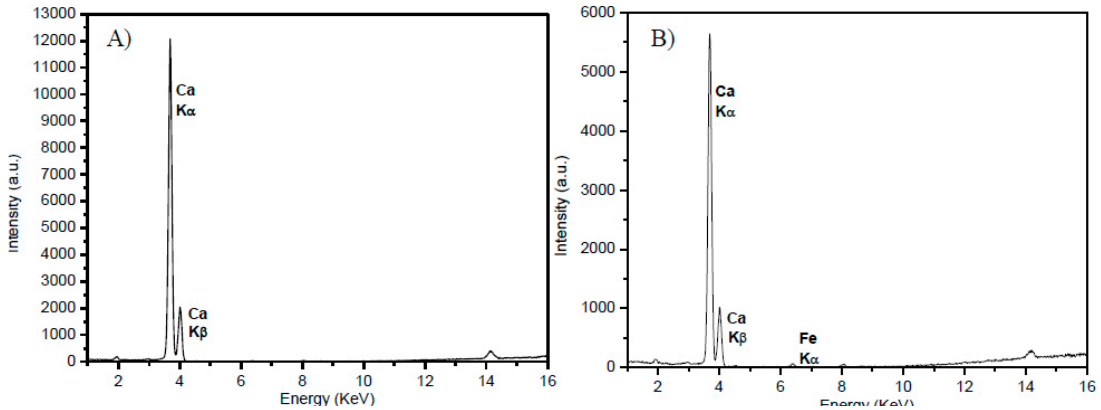

Figure 18. XRF spectra of **A)** specimen C1 point 1 and **B)** specimen D1 point 1.

By means of XRF, it was possible to assess that the signal of iron practically disappear in the case of calcite sample, while for dolomitic there is still a small signal, further confirming that for dolomite the removal of rust is more difficult.

To improve the performances of the treatments, the use of a different support respect to traditional based poultice cellulose has been tested: the support chosen is agar using the same formulation previously tested: SDT + 3.5% sodium carbonate with a pH of around 7. By using this new material, the treatment had a greater power of stain absorption, due to the high absorption capacity of the agar; moreover, it was possible to follow in real time the cleaning process (thanks to the transparency of poultice), without the need to stir the poultice, consequently changing the treatment conditions. This change resulted in a decrease of almost half the time of contact between the stone material and poultice. Below there is a time-line of such treatment.

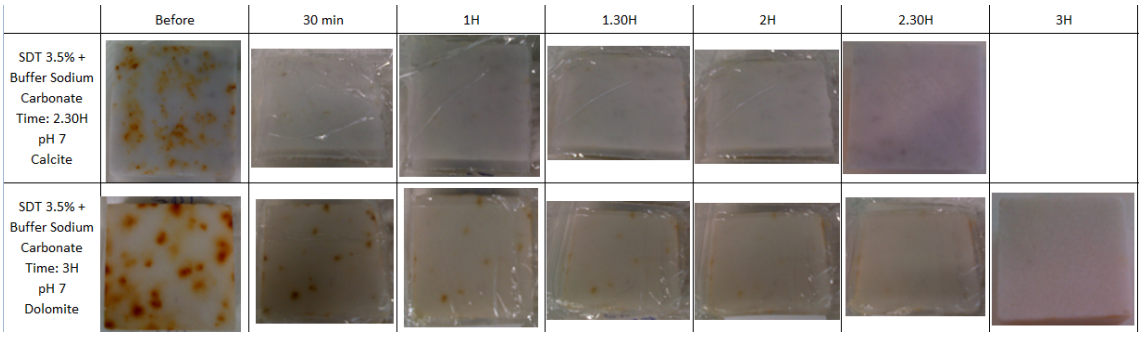

Figure 19. Timeline SDT 3.5% with agar poultice.

This treatment result in an effective cleaning of the stone material, thus confirming the qualities of this treatment with respect to the rust stains cleaning and also allowing full control of the treatment process.

A last improvement was tried in order to reduce the problem of sodium salts present in solution. It is not possible to reduce sodium deriving from SDT, but it is possible to act on buffer solution. This was obtained by using ammonium carbonate instead of sodium carbonate, used

in previous experimental procedures. Although some stains remained, these may be the result of poor contact between the surface and the poultice, since there were other patches of equal or even higher intensity removed. This can be seen in Figure 20 before and after for the two types of stone materials.

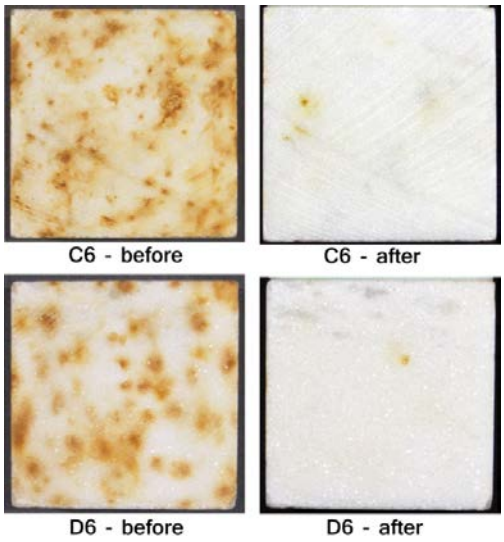

Figure 20. Before and after SDT 3.5% with agar poultice C6-D6 specimens.

The change of buffer resulted in decreasing the salts in solution. When examining the residues present in agar, in attenuated total reflectance (ATR) mode, traces of ammonium sulfate were found. Together with this compound, traces of sodium sulfate were also encountered, due to the decomposition of sodium dithionite [7].

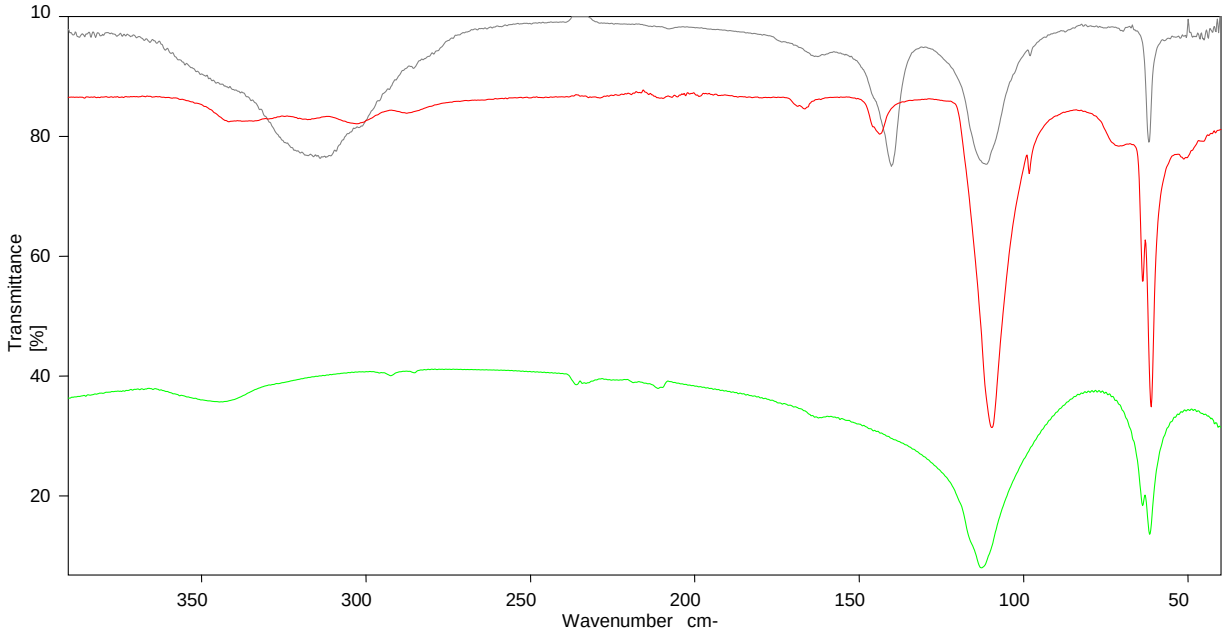

Figure 21. Infrared spectra (—) agar poultice powder SDT 3.5% buffered with ammonium carbonate (—), ammonium sulphate pattern (—) and sodium sulphate pattern.

Treatment repetition

Through XRF analysis was evident that in some cases the iron was still present, especially in dolomite stone. Therefore, the treatment that gave the best results in removing iron stains (SDT) was repeated. Samples chosen for this test were C5-D5 (agar poultice) and C1-D1 (cellulose poultice). The treatments were repeated in the same conditions as the previous.

After performing these treatments, XRF analysis was repeated in order to check if any improvement was made. In the Figure 22-A) the XRF spectrum for D1 sample treated with cellulose poultice + SDT/sodium carbonate is presented. Iron is almost absent, barely impossible to see in the spectra. The same happens in Figure 22-B, specimen D5 treated with the agar poultice + SDT/ammonium carbonate.

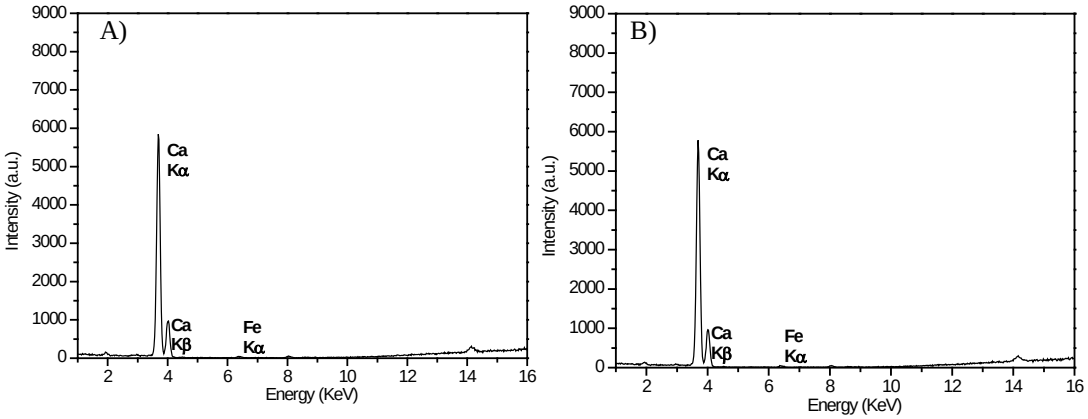

Figure 22. XRF spectra of **A)** specimen D1 point 1 and **B)** specimen D5 point 1.

3.3.2 Sodium Hexametaphosphate

The use of this cleaning agent, has not achieved the desired results. The pH of the solution was around 4/5, reason why a buffer was used, 30% ammonium solution was used to adjust the pH of the solution to about 7. The obtained results are reported in Figure 23.

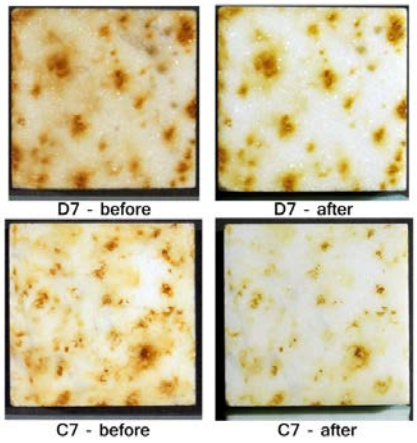

Figure 23. Before and After Sodium Hexametaphosfate 10% C7 - D7 specimens.

The concentration used in this treatment was 10% with a contact time of 2 hours. The concentration of 5% was not used because it was found that by using higher concentration (10%), satisfactory results were not obtained and only the superficial rust was removed.

An improvement to the treatment was tried by using agar poultice instead of cellulose poultice; however due to the hexametaphosphate deflocculants properties, it did not allow the typical agar gel from forming.

Table 7. Color measurements of the cleaned and unstained calcitic specimens.

Cleaned calcitic specimens				**Unstained calcitic specimens**			
Specimen - Point	L*	a*	b*	Specimen - Point	L*	a*	b*
C7 - 1	81,62	-0,47	1,88	**C17 - 1**	82,74	-0,70	-0,86
C7 - 2	51,77	19,07	29,97	**C17 - 2**	81,90	-0,78	-0,47
C7 - 3	67,22	11,64	28,52	**C17 - 3**	81,97	-0,61	-0,88
C7 - 4	70,59	7,71	20,47	**C17 - 4**	80,50	-0,72	-0,03

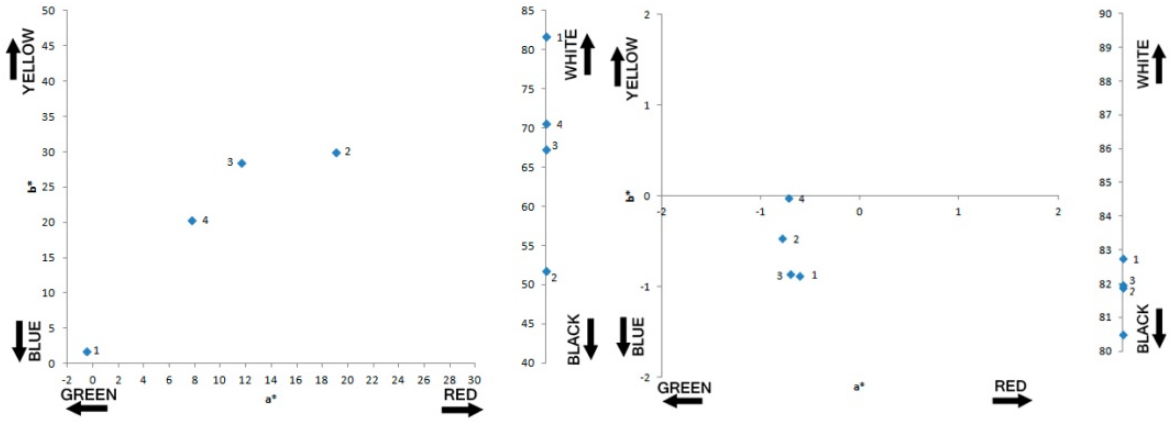

Figure 24. Values of the L*, a* and b* chromatic coordinates corresponding to the 2 different specimens (C7 and C17, respectively).

Table 8. Color measurements of the cleaned and unstained dolomitic specimens.

Cleaned dolomitic specimens				**Unstained dolomitic specimens**			
Specimen - Point	L*	a*	b*	**Specimen - Point**	L*	a*	b*
D7 - 1	82,55	0,77	9,77	**D17 - 1**	86,68	0,03	1,25
D7 - 2	48,33	26,72	38,64	**D17 - 2**	86,84	0,23	1,52
D7 - 3	55,57	23,11	41,42	**D17 - 3**	86,61	0,05	1,61
D7 - 4	58,02	22,39	42,65	**D17 - 4**	86,21	0,09	1,41

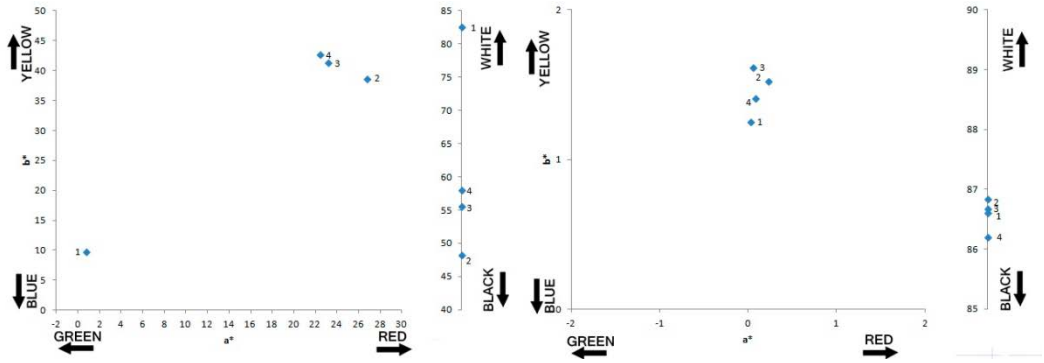

Figure 25. Values of the L*, a* and b* chromatic coordinates corresponding to the 2 different specimens (D7 and D17, respectively).

When the color measurements were made to prove what was seen in the surface photographs, the color only improved a little bit when compared with the reference specimens, as is possible to see in Figure 24 and Figure 25 and the Table 7 and Table 8.

Another analysis to confirm the fact that the orange color was still due to the presence of iron was the XRF, as is possible to see in Figure 26 where the spectra before and after treatment is showed for dolomitic specimen.

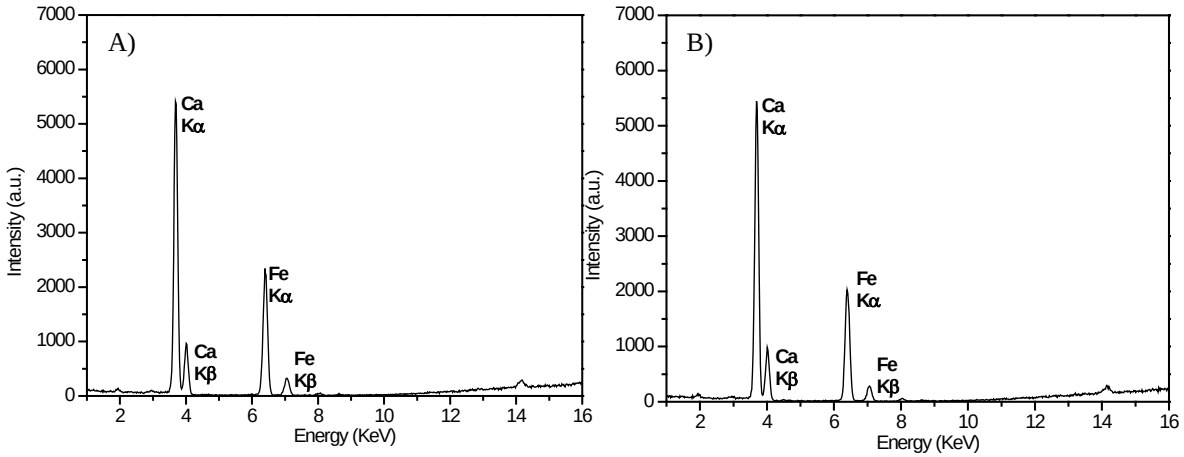

Figure 26. XRF spectra of **A)** specimen D7 point 1 before treatment and **B)** specimen D7 point 1 after treatment.

3.3.3 Ammonium Citrate

The results of the ammonium citrate cleaning intervention are presented in Figure 27. The surface cleaning was almost the same using either concentration of 2% or 5% solution. The contact time used in this case was longer compared to the other two treatments, but the results were completely not satisfying. The light colored yellow rust in the surface was removed, but the deep stains were not. The use of agar poultice instead the cellulose poultice did not improve the results.

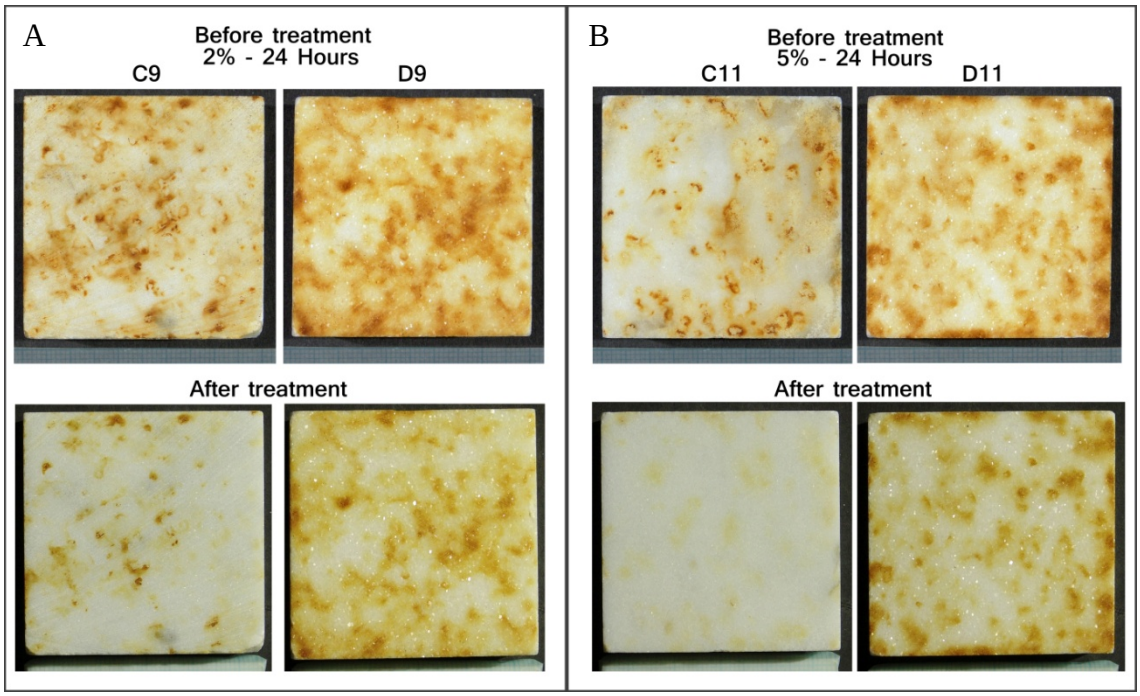

Figure 27. Comparison between treatments **A)** 2% - 24 hours **B)** 5% - 24 hours.

Color measurements proved what was seen in the surface photographs: the color only improved a little bit when compared with the reference specimens, as is possible to see in Figure 28 and Figure 29 and the Table 9 and Table 10.

Table 9. Color measurements of the cleaned and unstained calcitic specimens.

Cleaned calcitic specimens				**Unstained calcitic specimens**			
Specimen - Point	L*	a*	b*	**Specimen - Point**	L*	a*	b*
C9 - 1	76,16	0,41	9,53	**C16 - 1**	82,85	-0,68	-1,15
C9 - 2	66,60	8,65	21,34	**C16 - 2**	83,33	-0,66	-0,89
C9 - 3	72,51	4,98	26,32	**C16 - 3**	83,30	-0,67	-0,85
C9 - 4	71,17	5,8	20,46	**C16 - 4**	84,10	-0,70	-1,07

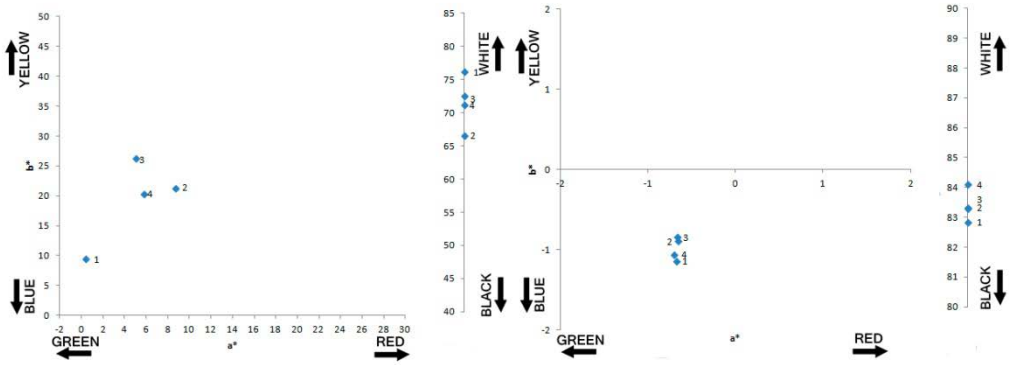

Figure 28. Values of the L*, a* and b* chromatic coordinates corresponding to the 2 different specimens (C9 and C16, respectively).

Table 10. Color measurements of the cleaned and unstained dolomitic specimens

Cleaned dolomitic specimens				Unstained dolomitic specimens			
Specimen - Point	L*	a*	b*	**Specimen - Point**	L*	a*	b*
D9 - 1	73,77	8,87	32,59	**D17 - 1**	86,68	0,03	1,25
D9 - 2	59,01	21,36	42,42	**D17 - 2**	86,84	0,23	1,52
D9 - 3	70,12	15,79	43,09	**D17 - 3**	86,61	0,05	1,61
D9 - 4	70,09	14,05	39,45	**D17 - 4**	86,21	0,09	1,41

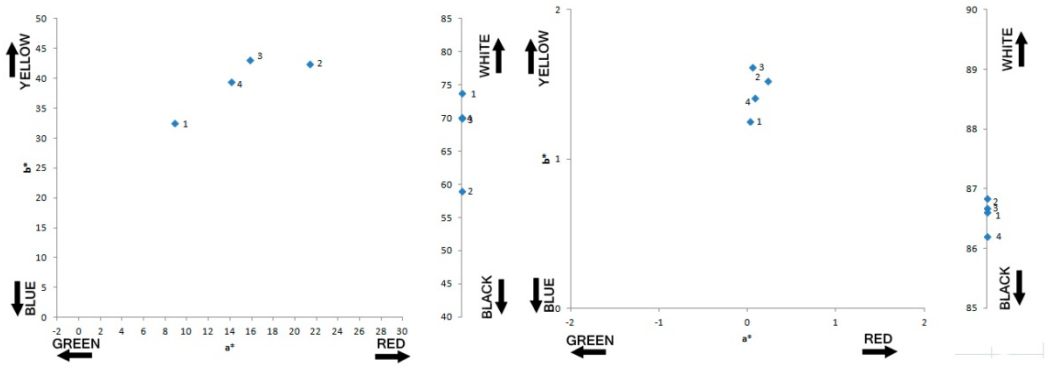

Figure 29. Values of the L*, a* and b* chromatic coordinates corresponding to the 2 different specimens (D9 and D17, respectively).

The confirmation of inadequate rust removal was confirmed by XRF, as is possible to see in Figure 30 where spectra before and after treatment are shown in a sample of dolomitic stone. In this case, it is possible to observe that the intensity of the iron signal is higher before than the after treatment.

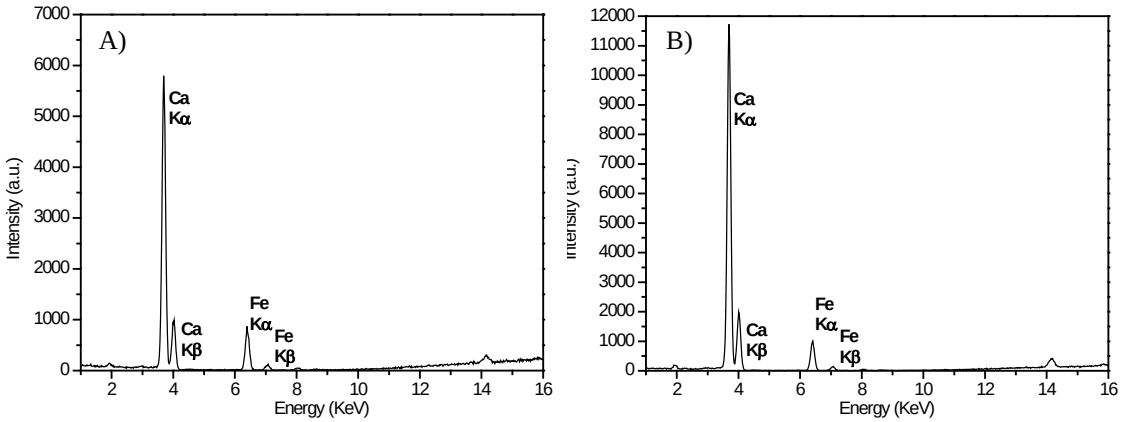

Figure 30. XRF spectra of **A)** specimen D7 point 1 before treatment and **B)** specimen D7 point 1 after treatment.

3.4 Comparison of water absorption tests (before and after)

After all the treatments were performed, the water absorption test was carried out. The short period of contact time when compared with the same test performed before the treatments did not shown conclusive data. Some of the values for the same treatment are different (in some cases, some specimens absorbed more after treatment and other less before treatment), as it is possible to conclude from Figure 31.

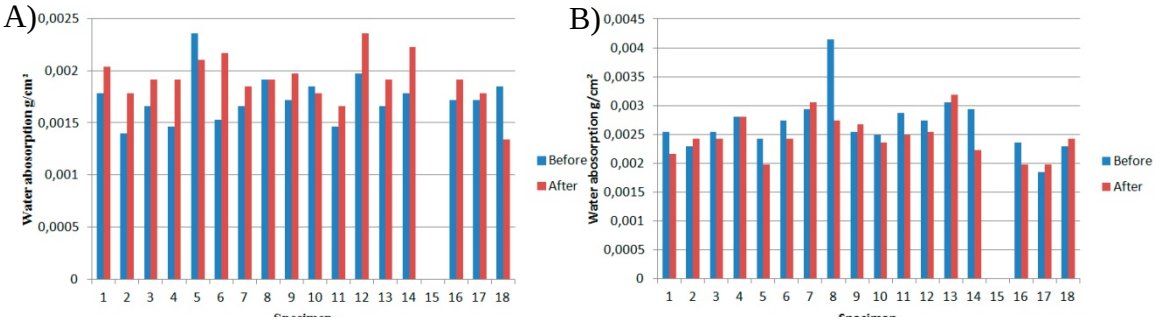

Figure 31. One minute water absorption g/cm^2 - before and after - **A)** Calcitic marble **B)** Dolomitic marble.

These unlikely results could be due to a great variety of external factors. In the case of long period of absorption time, the results obtained showed that the treatments affected the water absorption making it absorb less water than before the treatment. Despite this fact, one sample without rust (D18) was submitted to this test and it absorbed less water than the first time the test was performed. This could represent that some external factors can be behind this results such as: i) Relative humidity; ii) the process of excess water cleaning was not well removed; iii) Or the balance could have some mal function. The results are presented in the Figure 32 and Figure 33.

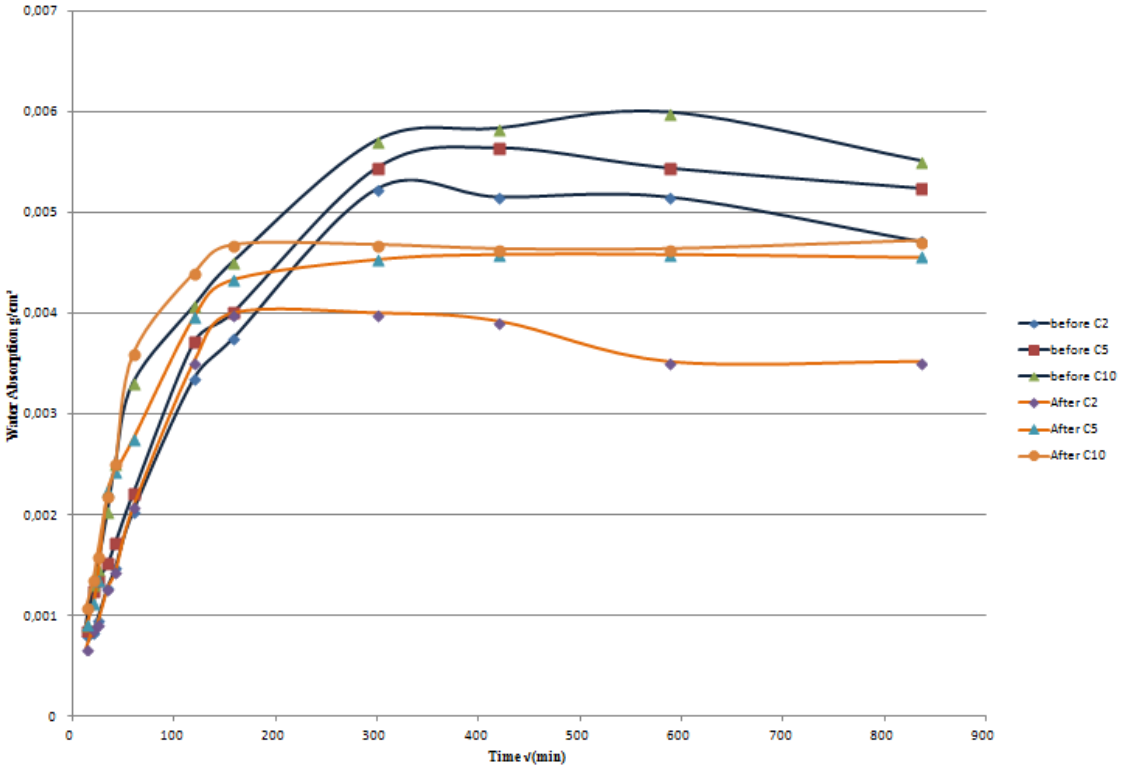

Figure 32. Long term water absorption g/cm$^{2.}$ – before and after - Calcite.

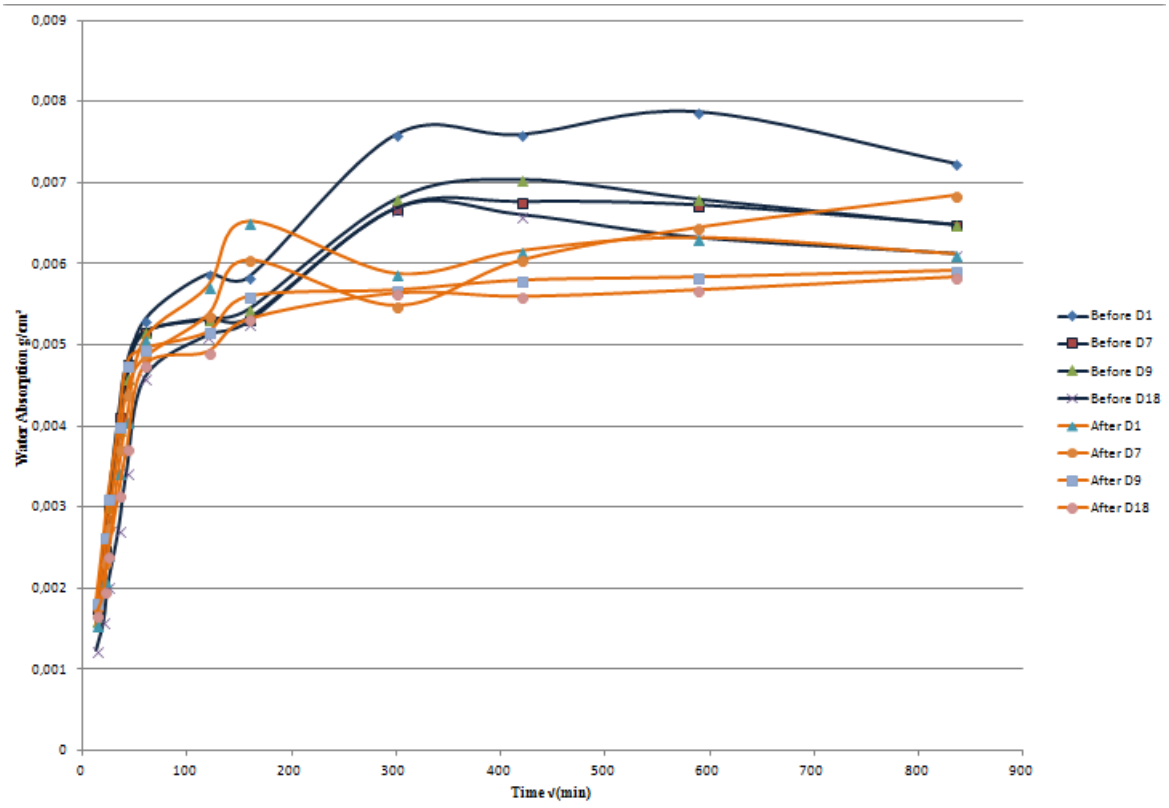

Figure 33. Long term water absorption g/cm$^{2.}$- before and after – Dolomite.

4. Conclusions

The study of a suitable, efficient and safe technique for the removal of rust from both calcitic and dolomitic marble was carried out. In order to achieve the objective, some promising chemical products reported in the literature were used, by exploring different application procedures. In order to make a better interpretation of the results obtained, analytical techniques were used to understand which are the advantages and disadvantages of the cleaning products used, having always in mind that the treatment should meet certain requirements including safety, harmfulness and applicability to real cases by restorers.

The use of sodium dithionite, despite the fact that the safety of this product to the operator is a bit harsh, proved to be an excellent product for rusted stone cleaning. It works as a reducing agent, making possible to wash away the iron from the stone.

A major problem for this treatment was the use of a correct buffer. A proper combination could prolong the cleaning agent life (which decomposes rapidly in the presence of oxygen) but also regulate the pH of the solution in contact with the stone material. After performing the FTIR analysis, sodium sulfate in the poultice was found. In order to reduce the amount of this compound, the buffer solution was changed from sodium hydrogen carbonate to ammonium carbonate, which allowed a reduction of sodium sulfates after cleaning, thus improving the safety and stability to the stone material.

The use of Hexametaphosphate proved to be unsuitable for this type of cleaning. It would be possibly suitable for other types of cleaning, such as the dissolution of gypsum, which forms over time on the marble surface.

Finally, the use of ammonium citrate showed better results than the previous chemical compound. This cleaning agent should be used when the rust stains are still in an initial state, where its intensity and deepness are low. As this is a less aggressive product, it should be suitable for those situations.

The application method of treatments also proved to have some importance, since depending on the method, different results were obtained. The use of agar as a poultice instead of the usual cellulose poultice, allows the operator to follow more effectively the evolution of the treatment without touching the poultice, which in sensitive substrates translates into an advantage.

In conclusion, depending on the case, with the execution of this work we can safely say that in the situation of deep rust it would be better to use a SDT 3.5%, buffered with Ammonium carbonate, applied with agar and followed by accurate washing of the stone surface, in order to remove all the undesired agents. If the rust stains are only superficial, various applications of Ammonium citrate buffered with ammonium solution applied with agar also produced good results.

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Appendices

APPENDIX 1. List of previous treatments on rust removal

Table 11. List of previous treatments on rust removal.

Treatments	Authors
Carboxylic acids including citric acid and salts	Stambolov and van Rheeden 1968, Matero and Tagle 1995
Oxalic acid	Stambolov 1968
Disodium EDTA	Stambolov 1968, Bone 1988, Alessandrini et al. 1984, Carter 1968
Thioglycolic acid	Thorn 1993, Stambolov and Van Rheeden 1968, Howie 1974
In the major part of this last cleaning agents a buffer was used	
Sodium citrate in 1957	Amoroso and Fassina 1983
EDTA In 1962	Plenderleight 1971
Citric acid, oxalic acid, and EDTA in 1976	Rinne 1976
Sodium citrate 1968	Stambolov 1968
AB57 – pH 8	Mora et al. 1984
Ammonium Thioglycolate – pH 8	Windholz 1983
Ammonium Thiosulphate	Stambolov and van Rheeden 1968
Citric Acid pH 3	MacLeod and North 1979, MacLeod 1987
EDTA pH 4	Alessandrini et al. 1984, Thorn 1993
EDTA pH 11	Thorn 1993
Sodium Thiosulphate	Stambolov and Van Rheeden 1968, Edos 1990
Sodium Gluconate pH 6	Stambolov and van Rheeden 1968, Edos 1990
Sodium Hydrosulfite pH 9	Merk 1981, Gilberg 1982, Barov 1987
Thioglycolic Acid	Stambolov 1968, Edos 1990, Howie 1974
Ammonium Citrate pH 9	Matero and Tagle 1995
Ammonium Citrate pH 6.5	Gale 1982
“Bio-Pack” and Hydrofluoric Acid pH 2.5	Sramek 1991
Versenol (EDTA)	Plenderleith 1955
Oxalic Acid, Citrate, and EDTA	Rinne 1976
Trisodium Citrate pH 8	Stambolov and van Rheeden 1968
Sodium dithionite	Stambolov (1968)
Sodium thiosulfate	Stambolov (1968)
Ammonium citrate buffered with ammonium hydroxide	Matero and Tagle (1995)
Ammonium thioglycolate	Thorn (2005)

APPENDIX 2. Experimental section

2.1. Specimens distribution

Table 12. Distribution of specimens according to the treatment.

Samples		Treatment	Concentration	Contact time	Poultice
C1	D1	SDT + sodium hydrogen carbonate	3.5%	6 hours	Cellulose
C2	D2	SDT + sodium hydrogen carbonate	3.5%	6 hours	Cellulose
C3	D3	SDT + sodium hydrogen carbonate	7%	3 hours	Cellulose
C4	D4	SDT + sodium hydrogen carbonate	7%	3 hours	Cellulose
C5	D5	SDT + Ammonium carbonate	3.5%	4 hours	Agar
C6	D6	SDT + Ammonium carbonate	3.5%	4 hours	Agar
C7	D7	Hexametaphosphate + Ammonium	10%	2 hours	Cellulose
C8	D8	Hexametaphosphate + Ammonium	10%	2 hours	Cellulose
C9	D9	Ammonium citrate + ammonium	2%	24 hours	Cellulose
C10	D10	Ammonium citrate + ammonium	2%	24 hours	Cellulose
C11	D11	Ammonium citrate + ammonium	5%	24 hours	Cellulose
C12	D12	Ammonium citrate + ammonium	5%	24 hours	Cellulose
C13	D13	SDT + sodium hydrogen carbonate	3.5%	6 hours	Cellulose
C14	D14	SDT + sodium hydrogen carbonate	7%	3 hours	Cellulose

Table 13. Function of the specimens.

Samples		Function
C15	D15	Cross-section
C16	D16	Pattern specimen
C17	D17	Pattern specimen
C18	D18	Pattern specimen

2.2. Experimental methods

Sodium dithionite solution preparation

Sodium dithionite solution was prepared using 200ml of distilled water and 7 grams of sodium dithionite to form a 3.5% solution. To prepare the 7% solution was used 14grams of sodium dithionite. Distilled water was under stirring while the reagent was added slowly to facilitate mixing. The buffer solution was prepared with sodium bicarbonate 1Molar in order to subsequently adjust the pH of the solution, adding it immediately after preparation to the sodium dithionite solution. After the preparation of the solution, for each specimen, 50ml was used mixed with cellulose or agar to form the poultice.

Sodium Hexametaphosphate solution preparation

Sodium hexametaphosphate solution was prepared using 100ml of distilled water and 10 grams of sodium hexametaphosphate to form a 10% (v/w) solution. Distilled water was under stirring

while the reagent was added slowly to facilitate mixing. To adjust the pH to the desired value, few drops of ammonium solution were added. After the preparation of the solution, for each specimen, 50ml was used mixed with cellulose to form the poultice.

Ammonium Citrate solution preparation

Ammonium citrate solution was prepared using 100 ml of distilled water and 5 grams of ammonium citrate to form a 5% (v/w) solution. The 2% (v/w) solution was prepared using 100ml of distilled water and 2 grams of ammonium citrate. The reagent was added slowly under stirring to facilitate mixing to distilled water. To adjust the pH to the desired value, few drops of ammonium solution were added. After the preparation of the solution, for each specimen 50 ml was used, mixed with cellulose to form the poultice.

Treatments application on the specimens

Prior to the application of treatments the surface of the stone was moistened to guarantee better contact with treatment, this condition was tested in trials, and found that it actually did better when the stone surface was wet. After making a homogeneous mixture of the poultice and the treatment, a thick layer was applied, covering it immediately afterwards with plastic film. After the contact time, the poultice was removed and stone surface was washed abundantly to remove any debris that could remain on the stone material surface.

Agar Preparation and gel application

To prepare the agar, the different solutions were heated up to 85ºC (checking accurately the temperature with a thermometer). Special attention was posed in the case of sodium dithionite, since it decomposes at temperatures higher than 90ºC. In this case was chosen not to heat so much the solution, and cover it with a aluminum foil, so that there was not so much evaporation of the solution. After the solutions were heated under stirring 3% (w/w) of agar was added to each solution. Stirring was continued until it became thicker. Then, the temperature was switched off and the gel was placed in a petri dish until cooling. After that the gel was cut and placed on soaked stone surface and covered with plastic film to prevent solution evaporation.

2.3. Materials

Stone Material

Calcitic marble or carrara marble is from Colonnata, near Carrara city. The grain size distribution is unimodal with rare coarser grains (500μm), the mean grain size is around 150 μm. The specimens were cut on a cutting table leaving it a flat surface.

Dolomitic mable or Sivec marble is from the quarries near the town Prilep in Macedonia. It is a white marble, hard and possesses a coarse grained around 400mm. The specimens were cut on a cutting table leaving it a flat surface.

Reagents

Ammonium carbonate - NH_4HCO_3 - from Riedel-de Haën;

Ammonium hydroxyde - NH_4OH - from Analyticals Carlo Erba;

Ammonium citrate dibasic - $HOC(CO_2H)(CH_2CO_2NH_4)_2$ - fom Fluka Analytical;

Sodium hydrogen carbonate - $NaHCO_3$ - from Fluka analytical;

Sodium dithionite – $Na_2S_2O_4$ - from Sigma-Aldrich;

Sodium Hexametaphosphate – $NaPO_3$ from CTS;

Poultice materials

Methyl Cellulose;

Agar from Sigma-Aldrich;

pH measurements

Measuring tapes – pH 1-10 from Carlo ERBA;

Electronic pH meter – Eutech instruments, PC 5000;

2.4. Apparatus

Infrared spectroscopy

FTIR analyses were carried out using a portable FTIR Bruker ALPHA, equipped with reflectance, diamond ATR and transmittance accessories. The software used was OPUS. Operating parameters: resolution 4 cm^{-1}, 256 scans, range 7500-400 cm^{-1}, background in reflectance mode on gold mirror.

X-Ray Fluorescence

X-Ray Fluorescence spectra were obtained using a portable XRF Bruker Tracer III-SD, with Artax software. A drawing was made in order to identify which was the position of the stone specimen. In Figure 33 is possible to observe how it was made. The external lines represent the plate where the specimens were place. The squares represent 3 different position of the specimen.

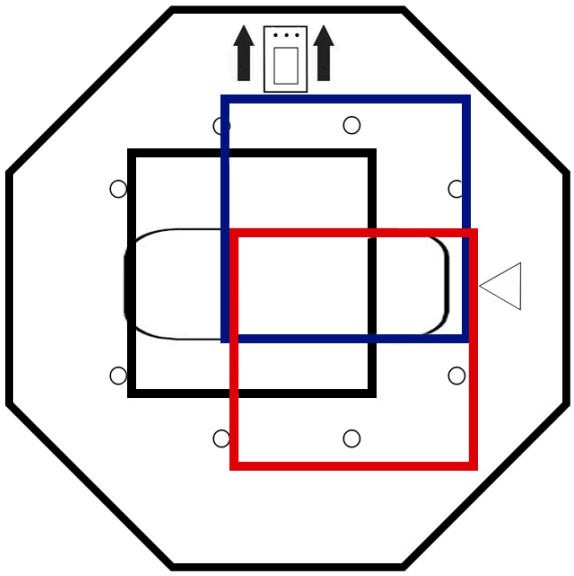


Figure 34. Template for XRF analysis .

SEM-EDS

SEM images were obtained using a FEI Quanta 200 with microprobe X-EDS.

X-Ray Diffraction

X-Ray diffractometer were obtained using a PANalytical diffractometer X'Pert PRO with radiation CuK□1= 1,545Å, operating at 40 KV, 30 mA, investigated range 2□3-70°, equipped with X' Celerator multidetector and High Score data acquisition and interpretation software was used directly on powders obtained by each sample.

Color measurements

Color measurements were performed according to the procedure described in European Standard EN15886 (2010) using the CIELAB 1976 method, with the standard illuminant D65 and observer 10°. The color coordinates L*, a* and b* were recorded for each selected point (Ø~8 mm), before and after treatments using a KONICA MINOLTA Spectrophotometer CM-700d, with Software SpectraMagic NX. The characterization of the samples was performed by using mask acetate sheets drawn in order to repositioning on the same are before and after treatments. In Figure 32, the mask used on color measurements and portable microscope process is reported.

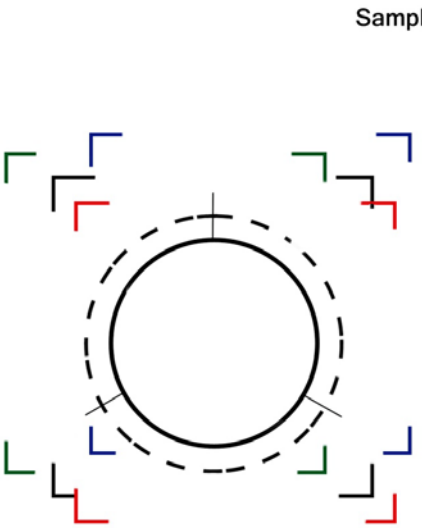


Figure 35. Template for the color measurments.

Four different areas in each specimen were chosen, in order to represent the most intense rust spots. For each point five measurements were performed in order to do an average. Each angle of different color represents the perimeter of the sample to be analyzed. By overlapping the different corners of the colors we were able to analyze different sample points.

In the centre of the circle the acetate sheet was cut so that there was not any interference between the material and the analysis performed. The three lines drawn in the acetate sheet, which, if united form a triangle were used so that the colorimeter head was easily positioned.

Digital portable microscope

Digital microscope pictures were obtained with a Digital portable microscope DG-3x, scalar. To positioning the equipment, a similar system used for color measurements was used.

Optical microscope

Camera Nikon D5-Fi1C

Microscope eclipse E-600 with Nikon y-FL.;

Stereo microscope

Microscope Zeiss 2000-C with digital camera DXM 1200F. To investigate the exact position before and after the treatment, an acetate mask represented in Figure 33 was made enabling to repeat the photograph in the same exact position.

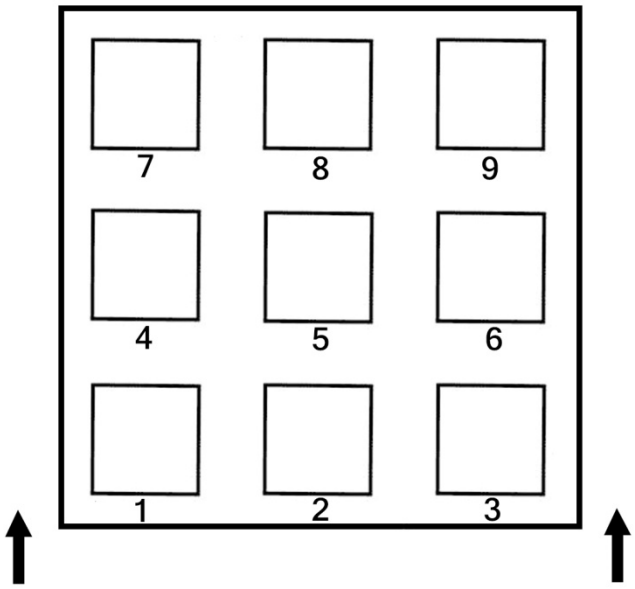


Figure 36. Template for the stereomicroscope photograps.

The square above the represented numbers corresponds to the area observed by optical microscope, remembering that these areas were cut so that there would be no interference with the images obtained. The outer square containing all the others corresponds to the perimeter of the specimen.

Surface photographs

Sony DSC-F828 camera;

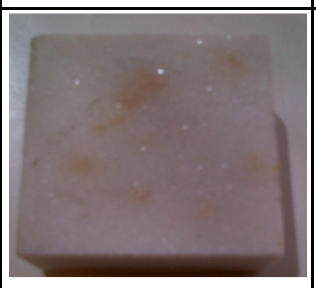
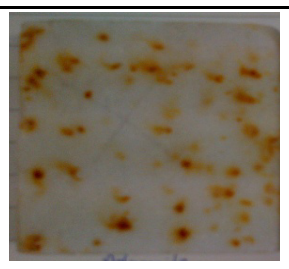
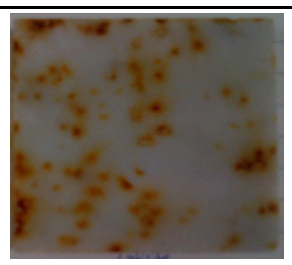
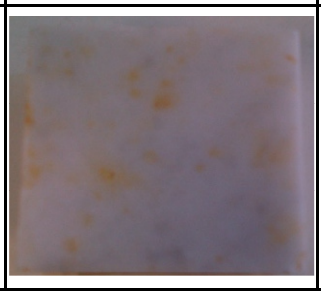
pH measurements

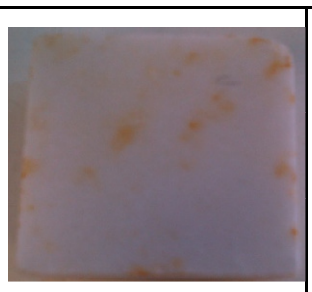
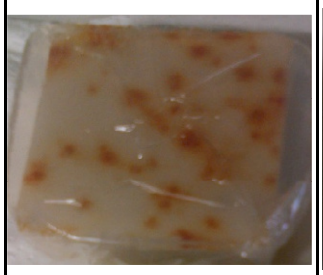
pH measurements were made with a Eutech instruments, PC 5000, pH Conductivity meter. Calibration was performed with pH 4.01, 7 and 9.21 buffered reference solutions.

Balance

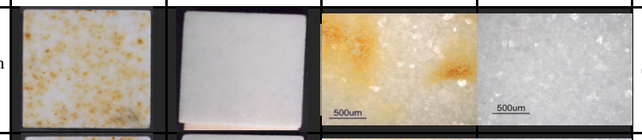
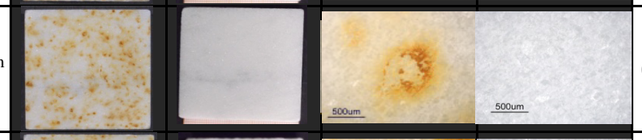
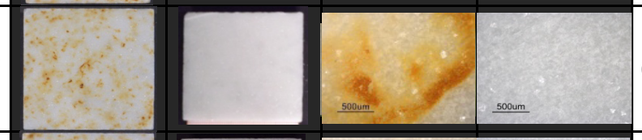
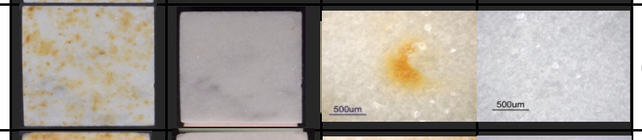
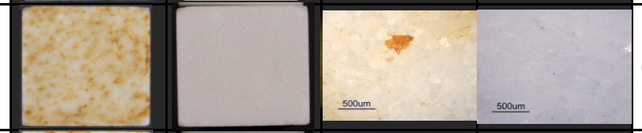
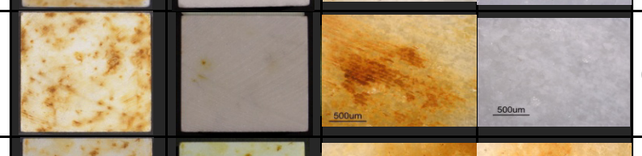
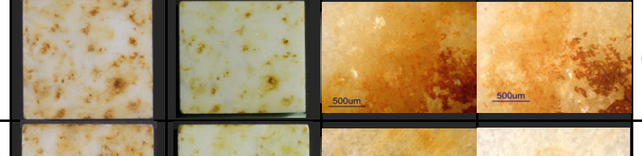
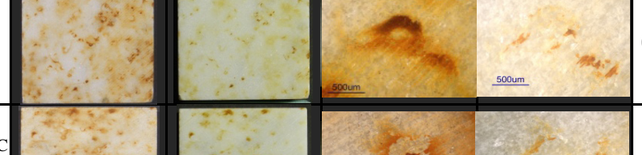
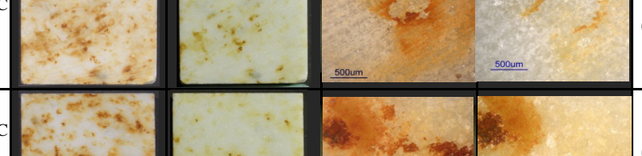
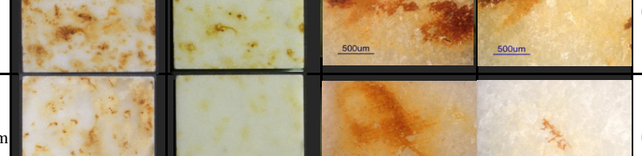
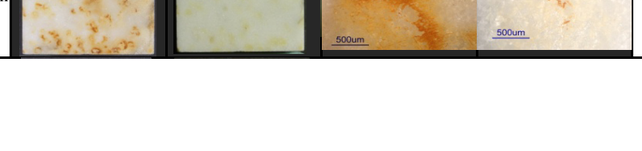
Kern EG 620-3NM

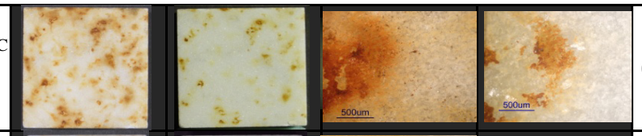
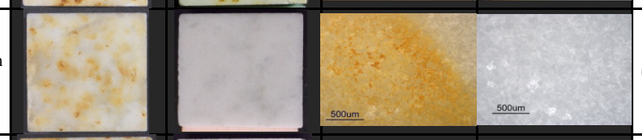
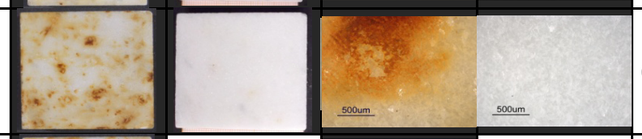
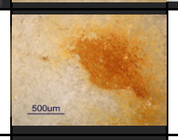
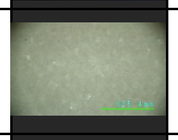
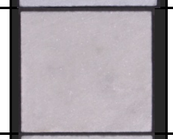
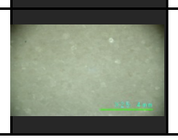
APPENDIX 3. Trials table

Treatment	Surface photography		Why this trial?	Observations
	Before	After		
SDT 3.5% + sodium bicarbonate Time: 6H pH ≈ 7 Dolomite	Not available		Was the first trial with this treatment to check how this treatment worked and to understand how it cleans.	Worked very well, same effect as the SDT with the buffer sodium carbonate. With FTIR analysis we still are able to see Sulphate, but in less quantity than the other buffer.
SDT 3.5% + Buffer Sodium Carbonate - Without weting the surface Time: 21H pH ≈ 7 Dolomite	Not available		To try and understand how the cleaning procedure worked in this conditions.	Despite the time that it took to the cleaning agent work, the final result was quite good. Only one very deep spot remained. With this, we could conclude that weting the surface is a important step in the cleaning process.
SDT 3.5% + Buffer Sodium Carbonate Time: 6 + 6H pH7/8 Calcite	Not available		Was done a first trial with SDT 3.5%, worked very well. But after a day, some of the Fe2+ (inside the stone) returned to Fe3+ state, presenting again some stains. So, this trial was to try to completly remove the Fe3+.	Completly removed the stains. So, if the stains are too deep, problably a second round of cleaning is needed.
SDT 3.5% + Buffer Ammonium Carbonate Time: 5H pH 7.5 Dolomite			Because we wanted to see if the formation of sodium sulphate was minimised by adding another compound that didn't had sodium in it. And if the cleaning was possible.	Worked very well, same effect as the SDT with the buffer sodium carbonate. With FTIR analysis we still are able to see Sulphate, but in less quantity than the other buffer.
SDT 3.5% + Buffer Ammonium Carbonate Time: 5H pH7.5 Calcite			Because we wanted to see if the formation of sodium sulphate was minimised by adding another compound that didn't had sodium in it. And if the cleaning was possible.	Worked very well, same effect as the SDT with the buffer sodium carbonate. With FTIR analysis we still are able to see Sulphate, but in less quantity than the other buffer.
Ammonium Citrate 5% + Buffer Amonium Time: 24H pH 7/8 Calcite	Not available		To try and see if the conditions presented in the literature were a appropriated	Works on light stains, but the deep stains remains. Indicated for Superfitial rust stains. That are more easy to remove.
Ammonium Citrate 2% + Buffer Amonium Time: 24H pH 7/8 Calcite	Not available		To try and see if the conditions presented in the literature were a appropriated	Worst than the 5% concentration, removed only some of the shadows around the stain.
Hexameta 10% + Buffer Ammonium Time: 2H pH 7/8 Calcite	Not available		To try and see this cleaning agent worked.	Removed light stains, but the deep stains remains. In this case worked more or less, but in the caracterized specimens didn't worked at all.
Hexameta 10% + Buffer Ammonium Time: 2H pH 7/8 Calcite	Not available		The point of this trial was to check if without weting the surface and if without covering the poultice with plastic film the result with hexameta 10% could be improved.	Removed light stains, but the deep stains remains. In this case worked more or less. There was no improvement's on the stain removal with this trial.

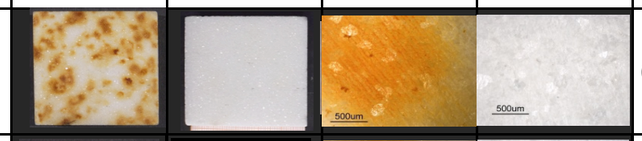
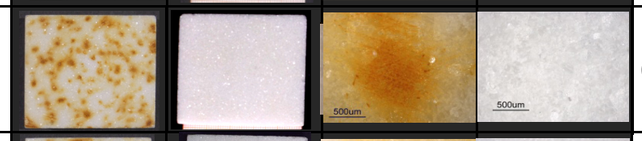
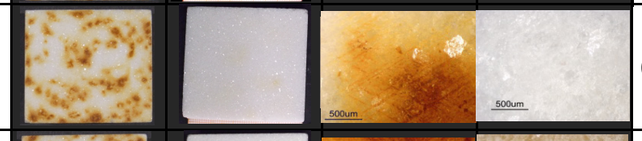
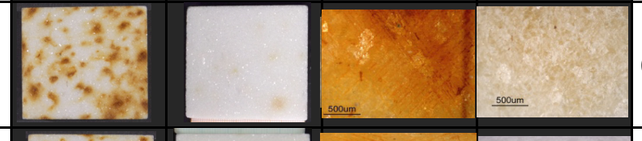
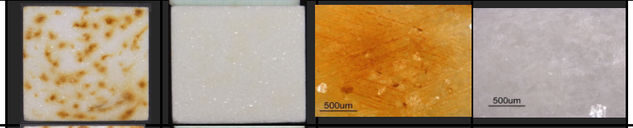
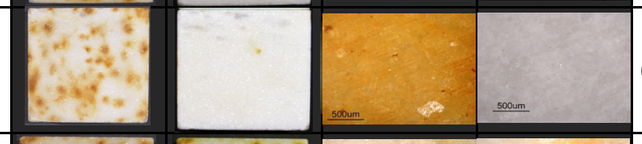
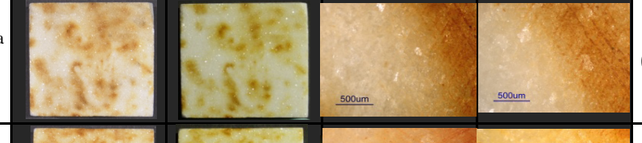
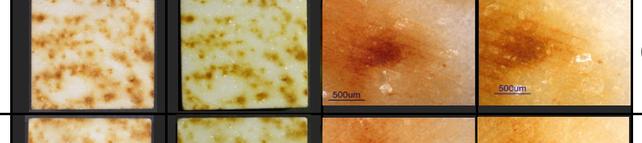
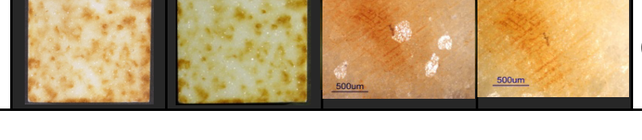
Hexameta 10% + Buffer Ammonium Time: 2H pH 7/8 Dolomite	Not available		To try and see how it worked on dolomite stone, in the same way that worked in Calcite.	Removed light stains, but the deep stains remains. In this case worked more or less, but in the caracterized specimens didn't worked at all.
Hexameta 10% + Buffer Ammonium Time: 2H surface not wet + 2H wet surface pH 7/8 Dolomite	Not available		To try and see how it worked on dolomite stone, and to see if not wetting the surface could change the final result. It didn't work so, i repeated the treatment but this time, wet the surface.	It didn't worked at all, maybe because the surface wasn't wet, we could see that this factor is important to a good cleaning. The repetition of the treatment even that the surface was wet, didn't improve the result.
Hexameta 5% + Buffer Ammonium Time: 2H + 2H pH 7/8 Calcite	Not available		To test the cleaning process at a lower concentration	Removed light stains, but the deep stains remained. In this case worked more or less.
AGAR Ammonium Citrate 5% + Buffer Amonium Time: 24H pH 7/8 Dolomite			To test if the cleaning process using Ammonium citrate could be improved.	In this case only the more superficial rust was removed. This technic proved to be equal as using a normal poultice.
AGAR Ammonium Citrate 5% + Buffer Amonium Time: 24H pH 7/8 Calcite			To test if the cleaning process using Ammonium citrate could be improved.	In this case only the more superficial rust was removed. This technic proved to be equal as using a normal poultice.

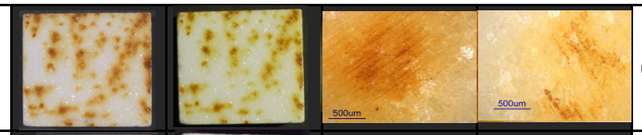
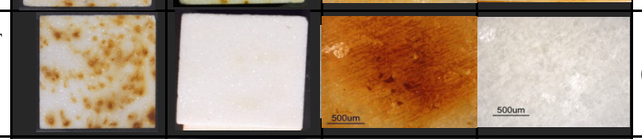
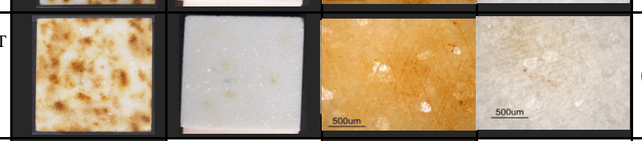
APPENDIX 4. Summary table - Calcite

Specimen	Treatment	Surface Photography		Stereo microscope		Water absorption 1minute (g/cm²)		Coloror measurements						XRF		Results (+ not efficient + + + + + efficient)
		Before	After	Before	After	Before	After	Before			After			Before	After	
								L*	a*	b*	L*	a*	b*			
C1	Cellulose poultice SDT 3.5% + Sodium bicarbonate 6H - pH≈7					0,00178344	0,0020382	79,338 74,482 75,022 75,656	0,51 4,692 3,956 2,946	12,986 29,268 24,49 26,256	82,136 82,642 82,464 82,816	-1,086 -1,084 -1,002 -1,076	1,942 2,04 1,996 1,756	Ca>Fe	Ca>>Fe	+ + + + +
C2	Cellulose poultice SDT 3.5% + Sodium bicarbonate 6H - pH≈7					0,00140127	0,0017834	83,65 79,402 78,126 73,378	-0,586 1,218 1,83 7,532	4,37 13,432 18,048 30,344	84,612 83,924 84,792 85,17	-0,752 -0,904 -0,898 -0,868	0,192 0,406 0,926 1,262	–	–	+ + + + +
C3	Cellulose poultice SDT 7 % + Sodium bicarbonate 3H - pH≈6					0,00165605	0,0019108	68,802 64,55 76,816 80,36	10,784 11,106 2,532 0,144	35,464 33,052 22,256 10,4	81,572 80,32 81,852 82,244	-1,402 -1,446 -1,534 -1,28	4,566 4,878 4,24 2,862	–	–	+ + + + +
C4	Cellulose poultice SDT 7 % + Sodium bicarbonate 3H - pH≈6					0,00146497	0,0019108	79,39 77,366 72,33 73,874	0,142 0,964 5,956 5,782	15,33 18,282 29,002 30,012	80,576 80,616 80,984 82,078	-0,832 -1,004 -1,018 -0,998	0,848 1,48 2,024 2,164	Ca>Fe	Ca>>Fe	+ + + + +
C5	Agar poultice SDT 3.5% + Ammonium carbonate 5H - pH≈7					0,00235669	0,0021019	81,224 78,336 79,046 79,946	1,12 4,066 3,502 1,1912	19,032 21,636 21,53 19,086	83,592 83,376 84,076 84,484	-0,602 -0,684 -0,632 -0,616	0,926 1,624 0,858 0,736	Ca>Fe	Ca>>Fe	+ + + + +
C6	Cellulose poultice SDT 3.5% + Ammonium carbonate 5H - pH≈7					0,00152866	0,0021656	81,572 55,618 57,346 70,002	0,172 19,276 17,18 10,674	10,784 35,972 35,158 31,314	85,4 82,296 83,718 85,458	-0,884 -0,782 -1,37 -0,906	0,932 6,31 3,388 1,078	–	–	+ + + +
C7	Cellulose poultice Hexa 10% + Ammonium 2H - pH 6/7					0,00165605	0,0018471	81,556 43,5 62,06 65,27	-0,37 23,546 18,694 11,608	7,056 30,634 41,144 27,24	81,622 51,766 67,216 70,594	-0,47 19,072 11,64 7,712	1,888 29,974 28,518 20,47	Ca>Fe	Ca>Fe	+
C8	Cellulose poultice Hexa 10% + Ammonium 2H - pH 6/7					0,00191083	0,0019108	69,808 62,73 64,248 75,342	11,464 15,676 14,89 5,528	38,434 37,96 37,714 24,334	76,934 75,062 76,212 80,336	2,282 2,298 2,598 1,072	22,268 21,308 20,456 12,162	–	–	+ +
C9	Cellulose poultice AC 2% + Ammonium 24H - pH ≈ 8.6					0,00171975	0,0019745	69,142 58,534 61,996 65,276	5,374 14,84 13,558 9,006	23,674 30,914 35,814 29,362	76,158 66,598 72,508 71,17	0,406 8,65 4,98 5,8	9,53 21,344 26,32 20,464	Ca>Fe	Ca>Fe	+ +
C10	Cellulose poultice AC 2% + ammonium 24H - pH ≈ 8.6					0,00184713	0,0017834	75,64 49,94 60,448 78,538	5,09 24,63 19,344 2,98	28,832 35,54 38,096 30,294	80,544 65,358 73,948 81,05	0,944 15,162 7,202 0,372	19,222 38,06 29,042 23,038	–	–	+ +
C11	Cellulose poultice AC 5% + ammonium 24H - pH ≈ 8.2					0,00146497	0,0016561	62,7 59,646 66,492 65,634	11,782 18,266 10,788 10,676	35,224 40,522 33,078 34,738	81,404 78,548 80,69 79,338	-0,748 0,808 -0,752 0,102	9,154 14,568 14,57 17,126	Ca>Fe	Ca>Fe	+ + +

C12	Cellulose poultice AC 5% + ammonium 24H - pH ≈ 8.2					0,00197452	0,0023567	78,702 49,998 48,506 54,62	0,888 24,018 22,61 21,044	16,876 37,136 33,142 42,478	84,032 65,15 69,098 68,716	-0,694 11,322 7,938 9,472	1,934 28,154 27,932 27,604	–	–	+ +
C13	Cellulose poultice SDT 3.5% + sodium bicarbonate 6H - pH ≈ 7					0,00165605	0,0019108	70,026 59,86 65,966 66,554	5,222 16,404 9,856 7,622	28,558 40,46 34,14 28,06	81,326 80,896 79,76 79,908	-0,908 -1,034 -1,014 -1,042	0,728 2,212 0,932 1,936	–	–	+ + + + +
C14	Cellulose poultice SDT 7% + sodium bicarbonate 3H - pH ≈ 6					0,00178344	0,0022293	81,252 58,064 53,858 48,69	0,378 19,948 22,51 22,284	11,498 42,952 38,356 33,052	83,134 79,088 81,13 81,612	-1,048 -0,894 -1,246 15,364	3,124 8,414 10,252 6,384	–	–	+ + + + +
C15	Destructive specimen		–		–	---	---	75,472 57,724 73,252 69,818	2,844 18,66 5,8 10,904	21,896 37,724 18,65 32,342	—			–	–	—
C16	References		–		–	0,00171975	0,0019108	82,85 83,332 83,298 84,102	-0,676 -0,658 -0,674 -0,702	-1,146 -0,892 -0,846 -1,068	—			–	–	—
C17	References		–		–	0,00171975	0,0017834	82,74 81,898 81,968 80,498	-0,698 -0,78 -0,612 -0,722	-0,862 -0,466 -0,884 -0,026	—			–	–	—
C18	References		–		–	0,00184713	0,0013376	82,936 81,358 79,536 82,042	-0,676 -0,698 -0,662 -0,66	-0,93 -0,844 -0,982 -0,864	—			–	–	—

APPENDIX 4. Summary table - Dolomite

Specimen	Treatment	Surface Photography		Stereo microscope		Water absorption 1minute (g/cm²)		Color measurements						XRF		Results (+ not efficient + + + + + efficient)
		Before	After	Before	After	Before	After	Before			After			Before	After	
								L*	a*	b*	L*	a*	b*			
D1	Cellulose poultice SDT 3.5% + Sodium bicarbonate 6H - pH≈7					0,00254777	0,0021656	84 63,532 53,456 52,32	0,546 18,308 24,474 26,38	13,854 41,46 40,736 42,108	87,04 86,282 85,952 86,994	-0,388 -0,428 -0,452 -0,552	3,08 7,714 8,336 6,378	Ca>Fe	Ca>>Fe	+ + + + +
D2	Cellulose poultice SDT 3.5% + Sodium bicarbonate 6H - pH≈7					0,00229299	0,0024204	85,11 68,858 79,754 52,32	0,596 14,63 3,596 26,38	7,042 40,788 18,558 42,108	86,498 86,632 87,014 85,722	-0,43 -0,492 -0,426 -0,512	2,942 5,094 3,154 5,808	—	—	+ + + + +
D3	Cellulose poultice SDT 7 % + Sodium bicarbonate 3H - pH≈6					0,00254777	0,0024204	73,132 67,76 63,176 58,248	10,89 16,276 20,892 23,108	33,052 43,532 44,028 44,54	85,546 84,466 85,778 86,486	-0,546 -1,044 -0,658 -0,706	6,282 13,516 7,948 6,152	—	—	+ + + +
D4	Cellulose poultice SDT 7 % + Sodium bicarbonate 3H - pH≈6					0,00280255	0,0028025	82,278 71,648 76,152 51,826	1,692 10,4 5,766 22,296	17,752 33,79 24,512 37,044	85,402 84,528 85,38 77,606	-0,436 -0,6 -0,608 3,266	4,684 8,834 6,756 20,306	Ca>Fe	Ca>>Fe	+ + +
D5	Agar poultice SDT 3.5% + Ammonium carbonate 5H - pH≈7					0,00242038	0,0019745	81,182 66,586 62,67 71,674	2,652 15,918 16,706 9,996	16,342 42,012 39,738 33,468	86,438 86,382 86,504 86,288	-0,116 -0,064 -0,07 -0,212	4,224 4,04 4,466 5,738	Ca>Fe	Ca>>Fe	+ + + + +
D6	Cellulose poultice SDT 3.5% + Ammonium carbonate 5H - pH≈7					0,00273885	0,0024204	68,584 64,21 64,156 63,472	12,358 14,334 14,89 14,89	32,496 34,064 35,432 35,432	86,764 86,6 83,388 86,198	0,07 0,048 1,364 0,024	2,792 3,282 8,384 3,936	—	—	+ + + +
D7	Cellulose poultice Hexa 10% + Ammonium 2H - pH 6/7					0,00292994	0,0030573	81,824 48,114 54,77 58,142	1,126 25,952 23,158 21,768	13,042 37,612 40,074 41,38	82,55 48,328 55,568 58,018	0,772 26,724 23,108 22,394	9,768 38,636 41,418 42,652	Ca>Fe	Ca>Fe	+ +
D8	Cellulose poultice Hexa 10% + Ammonium 2H - pH 6/7					0,00414013	0,0027389	71,4 52,676 56,696 55,1	7,532 21,006 17,674 16,658	30,276 39,37 36,546 33,848	73,374 54,938 59,894 55,608	5,84 20,53 16,538 17,184	28,256 40,144 37,232 35,066	---	---	+ +
D9	Cellulose poultice AC 2% + Ammonium 24H - pH ≈ 8.6					0,00254777	0,0026752	70,432 55,04 66,862 64,792	11,094 23,898 17,48 17,992	34,552 42,748 42,78 41,982	73,768 59,006 70,12 70,086	8,874 21,356 15,786 14,052	32,588 42,418 43,088 39,446	Ca>Fe	Ca>Fe	+
D10	Cellulose poultice AC 2% + ammonium 24H - pH ≈ 8.6					0,00248408	0,0023567	77,81 72,194 66,33 67,536	4,252 8,388 14,942 13,734	27,806 28,206 41,338 38,13	81,77 74,68 72,294 76,392	1,774 7,436 10,47 6,6	21,172 26,514 37,136 27,836	—	—	+ +
D11	Cellulose poultice AC 5% + ammonium 24H - pH ≈ 8.2					0,00286624	0,0024841	78,86 70,062 72,984 66,68	3,134 10,006 8,18 14,332	21,354 34,29 34,988 40,392	82,676 74,864 78,612 69,08	1,294 6,62 4,774 12,934	15,456 30,136 28,434 37,612	Ca>Fe	Ca>Fe	+ +

D12	Cellulose poultice AC 5% + ammonium 24H - pH ≈ 8.2					0,00273885	0,0025478	78,66 50,206 65,656 63,298	4,656 27,954 19,288 21,68	28,494 41,174 44,88 50,414	81,798 53,676 70,046 68,97	1,726 26,48 15,216 15,754	20,534 41,48 42,54 43,462	—	—	+ +
D13	Cellulose poultice SDT 3.5% + sodium bicarbonate 6H - pH ≈ 7					0,00305732	0,0031847	66,54 57,554 63,404 60,212	17,42 19,598 19,156 22,84	47,16 40,744 43,794 48,26	86,174 84,19 86,716 86,35	-0,572 -0,202 -0,714 -0,542	8,574 13,488 8,93 7,094	—	—	+ + + + +
D14	Cellulose poultice SDT 7% + sodium bicarbonate 3H - pH ≈ 6					0,00292994	0,0022293	73,208 46,932 45,078 47,558	7,564 25,928 24,132 26,724	32,48 41,268 35,87 41,374	84,746 79,926 80,826 81,418	-0,566 0,508 0,48 0,338	6,526 18,274 16,844 17,34	—	—	+ + + +
D15	Destructive specimen		—		—	0,00267516	—	78,996 66,976 63,112 68,216	3,702 14,912 18,948 14,606	23,744 39,51 40,574 40,004	—			—	—	—
D16	References		—		—	0,00235669	0,0019745	82,85 83,332 83,298 84,102	-0,676 -0,658 -0,674 -0,702	-1,146 -0,892 -0,846 -1,068	—			—	—	—
D17	References		—		—	0,00184713	0,0019745	82,74 81,898 81,968 80,498	-0,698 -0,78 -0,612 -0,722	-0,862 -0,466 -0,884 -0,026	—			—	—	—
D18	References		—		—	0,00229299	0,0024204	82,936 81,358 79,536 82,042	-0,676 -0,698 -0,662 -0,66	-0,93 -0,844 -0,982 -0,864	—			—	—	—